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THE PHYSICO-CHEMICAL INVESTIGATION OF SYSTEMS THAT CONTAIN IODINE CHLORIDE OR BROMIDE AND METALLIC HALIDES

V. RESEARCH ON NITROBENZENE SOLUTIONS OF THE KBr-IBr AND $AlBr_3$-IBr SYSTEMS

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The use of iodine bromide as a solvent was first studied in the publications of the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences.

The electrical conductivity of solutions of potassium bromide, potassium iodide, and aluminum bromide in iodine bromide was measured [1]. The results of measurements showed that aluminum bromide is readily soluble in iodine bromide, whereas potassium bromide and iodide are only very slightly soluble in it – no more than 7 - 8 mol. %, somewhat as the potassium halides are poorly soluble in iodine chloride.

As Ya. A. Fialkov and K. Ya. Kaganskaya [2] demonstrated, potassium chloride dissolves fairly readily in a nitrobenzene solution of iodine chloride, whereas KCl is entirely insoluble in pure nitrobenzene.

In their investigations of nitrobenzene solutions of iodine chloride and potassium chloride, and of iodine chloride with aluminum chloride, these authors showed that potassium and aluminum chlorides form coordination compounds with iodine chloride, as indicated by the solubility of potassium chloride in nitrobenzene in the presence of iodine chloride, and by the increase in conductivity and decrease in the depression of nitrobenzene solutions of ICl when KCl or $AlCl_3$ are added to them.

In their study of electrolysis and ion transfer in these systems, Fialkov and Kaganskaya [3] came to the conclusion that the coordination compound $K[ICl_2]$ is formed in the ICl – KCl – $C_6H_5NO_2$ system, i.e., the formula accepted in the literature for this compound is confirmed.

These authors proposed the formula $I[AlCl_4]$ for the coordination compound formed in the ICl – $AlCl_3$ – $C_6H_5NO_2$ system, because of the fact that upon electrolysis aluminum is transferred to the anode, whereas iodine is evolved at the cathode.

This research makes apparent the interest in studying analogous systems with bromides in order to ascertain whether the same rules apply in bromide systems as hold good in chloride systems.

With this in view, the IBr – KBr – $C_6H_5NO_2$ and IBr – $AlBr_3$ – $C_6H_5NO_2$ systems were investigated by the conductivity, cryoscopic, and ion-transfer methods.

Research Materials and Methods

The iodine bromide was prepared in a flask with a ground-glass stopper. To a weighed quantity of bromine [4], purified, dried over P_2O_5, and distilled, there was added the calculated quantity of iodine, triple-sublimed from a mixture of KI and BaO and desiccated over solid alkali.

After the reaction, the flask and its contents were warmed over a water bath with a temperature of 45°. The ground glass-stopper was replaced by a previously fitted asbestos stopper with a thermometer, and the crystallization temperature of the iodine bromide was measured.

The crystallization temperature of the product prepared by us was 40°. According to the literature, iodine bromide fuses at 40-41°.

The potassium bromide was purified by recrystallization and desiccation at 150-160°.

The aluminum bromide was prepared from purified bromine and aluminum shavings, followed by double distillation. The electrical conductivity of the aluminum bromide could not be determined.

The nitrobenzene was purified as described in our previous reports [2].

Measurement of specific conductivity was effected in a vessel with platinum (not platinized) electrodes. The temperature variation of the water thermostat did not exceed ± 0.1°.

The electrolyte was prepared directly in the vessel used for measuring conductivity.

Cryoscopic measurements were made in a Beckmann apparatus with ground-glass stoppers. After determining the freezing point of the nitrobenzene, we added a weighed amount of iodine bromide to it, measured the ensuing lowering of the freezing point, then added a weighed amount of potassium bromide or aluminum bromide, and again determined the lowering of the freezing point.

A U-tube served as the vessel used in electrolysis. We used the vessel described in the reports of V.A.Izbekov [5] to investigate ion transfer. Platinum electrodes were used. Electrolysis was effected at a voltage of 40-45 v; the current ranged from 2 to 3 milliamp. The test lasted 48 hours.

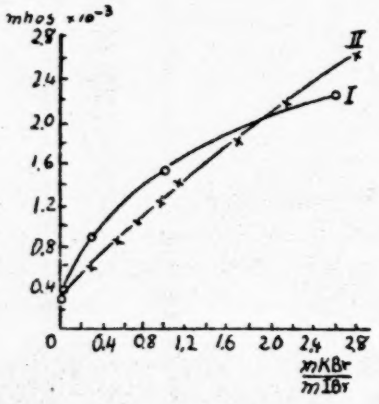

Fig. 1. Specific conductivity of the IBr – KBr – $C_6H_5NO_2$ system.

1- $\frac{IBr}{C_6H_5NO_2} = \frac{1}{11.28}$;

2- $\frac{IBr}{C_6H_5NO_2} = \frac{1}{23.99}$

1. IBr – KBr – $C_6H_5NO_2$

a) Specific Conductivity

Measurements of the specific conductivity of this system were made at 25° for two molar ratios of IBr to $C_6H_5NO_2$: 1:11.28 (I) and 1:23.99 (II).

Potassium bromide is insoluble in nitrobenzene, but in a nitrobenzene solution of iodine bromide the solubility of potassium bromide rises to about 0.5 mole % KBr per mole of IBr.

The results of these conductivity measurements are given in Table 1 and Fig. 1.

The conductivity of the IBr – KBr – $C_6H_5NO_2$ system rises with the concentration of KBr for a given IBr: $C_6H_5NO_2$ ratio; the same phenomenon was observed in the similar ICl – KCl – $C_6H_5NO_2$ system.

When we compare the conductivities at

TABLE 1

Weight of $C_6H_5NO_2$, g	Weight of IBr, g	Weight of KBr, g	Molar ratio IBr:KBr	$\kappa \cdot 10^3$
	Series I: Molar Ratio IBr:$C_6H_5NO_2$ = 1:11.28			
7.2270	1.0774	–	–	0.28
7.2270	1.0774	0.0207	1:0.034	0.89
7.2270	1.0774	0.0656	1:0.106	1.57
7.2270	1.0774	0.1654	1:0.267	2.24
	Series II: Molar Ratio IBr:$C_6H_5NO_2$ = 1:23.99			
25.0756	1.7577	–	–	0.29
25.0756	1.7577	0.0260	1:0.026	0.60
25.0756	1.7577	0.0569	1:0.056	0.87
25.0756	1.7577	0.0750	1:0.074	1.05
25.0756	1.7577	0.0957	1:0.095	1.25
25.0756	1.7577	0.1136	1:0.112	1.43
25.0756	1.7577	0.1784	1:0.176	1.76
25.0756	1.7577	0.2211	1:0.214	2.18
25.0756	1.7577	0.2886	1:0.285	2.67

constant KBr:IBr ratios, we find that at first the solutions with higher nitrobenzene concentrations have a higher conductivity; as the concentration of KBr rises – beginning with a KBr:IBr molar ratio of about 0.2, the order of conductivities changes, and the solutions with a higher dilution of nitrobenzene are more conductive.

The conductivity of this system is of the same order of magnitude (10^{-3} mho), but somewhat less than that of the ICl – KCl – $C_6H_5NO_2$ system.

b) Cryoscopic Investigation of the IBr – KBr – $C_6H_5NO_2$ System

The results of the cryscopic tests of this system are shown in Table 2.

When potassium bromide is added to the nitrobenzene solution of IBr, not only is the depression not increased, but it even drops (in all instances Δt_2 was smaller than Δt_1), as was the case in the ICl – KCl – $C_6H_5NO_2$ system [2].

This indicates that the process of formation of a coordination compound is linked with the dissolution of KBr in the nitrobenzene solution of IBr; this is accompanied by a reduction in the aggregate number of particles.

We assumed that the compound KBr·IBr, already described in the literature, is formed in the solution, i.e., that one mole of IBr combines with one mole of KBr. But since this should not entail any appreciable change* in the number of particles in the solution, and hence there should be no change in the depression of the solution, the lessening of the depression may be explained as due to the fact that the KBr-IBr compound formed in the solution is in the associated state.

Starting with the hypothesis that a compound with the formula KBr.IBr is formed in the solution, we calculated the molecular weight of this compound for solutions of different concentrations, as has been described in one of our previous reports on the cryoscopic investigation of the ICl – KCl – $C_6H_5NO_2$ system [2].

As may be seen in the data of Table 2, increasing the KBr concentration in the solution results in an increase in the molecular weight of the coordination compound KBr·IBr; the association factor, computed from the ratio $M_{comp.}:M_{theor.}$,

*Such a change in the number of particles in the solution can be caused only by a difference in the degree of electrolytic dissociation of the IBr· and KBr·IBr in nitrobenzene solutions.

Table 2

Cryoscopy of the IBr – KBr – $C_8H_5NO_2$ System*

IBr:$C_8H_5NO_2$ Molar Ratio: 1:46.01

Test No.	Weight of $C_8H_5NO_2$ g	Weight of IBr g	Δt_1°	Weight of KBr g	IBr:KBr Molar ratio	Δt_2°	Δt_3°	Computed quantity of $MIBr_2$ g	Molecular weight of coordination compound	$\frac{M_{comp.}}{M_{theor.}}$
1	17.3686	0.6347	1.01	0.0379	1:0.104	0.97	0.07	0.1038	583.11	1.78
2	17.3686	0.6347	1.01	0.0758	1:0.208	0.90	0.10	0.2076	816.39	2.50
3	17.3686	0.6347	1.01	0.1014	1:0.278	0.86	0.13	0.2778	840.32	2.57
4	17.3686	0.6347	1.01	0.1235	1:0.338	0.80	0.14	0.3383	950.23	2.91
5	17.3686	0.6347	1.01	0.1614	1:0.442	0.83	0.17	0.4421	1022.6	3.13

rises from 1.7 to 3.1. The conductivity of the IBr – KBr – $C_8H_5NO_2$ system increases as well.

Thus, it may be assumed that the associated molecules of the coordination compound undergo electrolytic dissociation, as in the analogous chloride system.

c) Research on Ion Transfer in the IBr – KBr – $C_8H_5NO_2$ System

It was found during the electrolysis of this system and the study of its ion transfer that a brown deposit is formed at the cathode. This deposit was washed with nitrobenzene or ether, after which there remained on the electrode a small quantity of an almost colorless, powdery deposit that was readily soluble in water, forming a highly alkaline solution. This demonstrates that potassium is evolved at the cathode.

The cathodic deposit also includes potassium bromide, as may be detected by its reaction with silver nitrate.

After the ion-transfer experiments, the anode, cathode, and middle portions of the liquid were weighed, treated with a saturated aqueous solution of SO_2, and analyzed.

Table 3

Ion Transfer in the IBr – KBr – $C_8H_5NO_2$ System

Test No.	Composition of the tested IBr:KBr $C_8H_5NO_2$ solution in moles	Cu deposited in the coulomb meter, g	substance measured	Solution after Electrolysis: cathode portion			middle portion			anode portion		
				expected reading g.	found, g	Δ g	expected reading, g	found, g	Δ g	expected reading g	found, g	Δ g
1	1:0.215 / 7.33	0.0858	K	0.0646	0.1273	+0.0627	0.0355	0.0354	-0.0001	0.0678	0.0054	-0.0624
			I	0.9147	0.6765	-0.2382	0.5360	0.5365	+0.0005	1.0228	1.2606	+0.2378
			Br	0.7459	0.4615	-0.2844	0.4104	0.4096	-0.0008	0.7832	1.0689	+0.2857
2	1:0.233 / 7.78	0.0789	K	0.0734	0.1210	+0.0476	0.0327	0.0323	-0.0004	0.0629	0.0152	-0.0477
			I	1.0299	0.8122	-0.2177	0.4593	0.4595	+0.0002	0.8819	1.0991	+0.2172
			Br	0.7949	0.5874	-0.2075	0.3545	0.3537	-0.0008	0.6806	0.8871	+0.2065

*Δt_1° is the lowering of the freezing point of IBr solutions in nitrobenzene; Δt_2° is the same quantity for solutions of IBr and KBr; Δt_3° is the depression computed for solutions of the coordination compound KBr·IBr; and $M_{theoret.}$ is the molecular weight of this coordination compound.

The potassium was determined as potassium sulfate, the total iodine plus bromine was determined by the Volhard method, and the iodine was determined by Winckler's oxidation method.

The results of the ion-transfer experiments are listed in Table 3.

The figures in Table 3 indicate that almost all the potassium moves to the cathode portion of the electrolyte. The percentage of bromine and iodine rises in the anode portion.

Computation of the number of equivalents of potassium transferred to the catholyte, and of iodine and bromine transferred to the anolyte yields the following values for Test No. 1: 1.60 milliequivalents for potassium, 1.77 for iodine, and 3.56 for bromine; i.e., for every equivalent of potassium transferred to the catholyte, one equivalent of iodine and two equivalents of bromine are transferred to the anolyte. The data of Test No. 2 yield the same ratios.

This is corroboration of the fact that the composition of the coordination compound formed in the nitrobenzene solution is represented by the formula $K[IBr_2]$.

The experimental data cited demonstrate that iodine bromide and potassium bromide combine in a nitrobenzene solution to form a complex molecule. This is testified to by the following facts: the solubility of potassium bromide in nitrobenzene in the presence of iodine bromide; the rise in conductivity of the ternary system as the concentration of potassium bromide is increased, and the smaller depression observed in the $IBr - KBr - C_6H_5NO_2$, as compared with the $IBr - C_6H_5NO_2$ system.

The transfer of potassium to the cathode and its deposition there, the transfer of iodine and bromine to the anode, and the quantitative results of electrolysis all indicate that the coordination compound formed in the nitrobenzene solution has the composition of $KBr \cdot IBr$ and the structure of $K[IBr_2]$.

2. The $IBr - AlBr_3 - C_6H_5NO_2$ System

a) Specific Conductivity

The conductivity of this system was measured at 25° for two $IBr:C_6H_5NO_2$ molar ratios - 1:7.26 (I) and 1:25.03 (II).

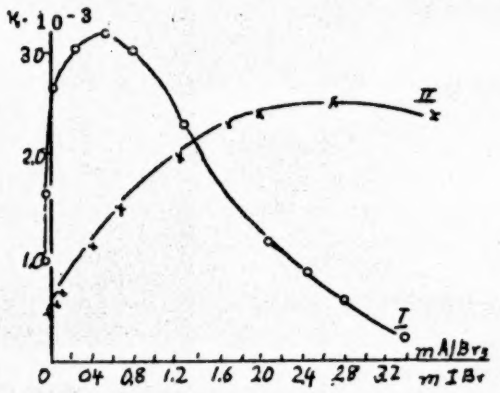

Fig. 2. Specific conductivity of the $IBr - AlBr_3 - C_6H_5NO_2$ System.

$$I - \frac{IBr}{C_6H_5NO_2} = \frac{1}{11.28};$$

$$II. \quad \frac{IBr}{C_6H_5NO_2} = \frac{1}{23.99}$$

The results obtained are shown in Table 4 and Fig. 2.

As these data indicate, the conductivity isotherm of solutions with higher nitrobenzene concentrations passes through a maximum at an $AlBr_3:IBr$ ratio of approximately 0.63; at the higher dilution of nitrobenzene a conductivity maximum is noted only in the region of high $AlBr_3$ concentrations.

In this respect the conductivity isotherms of this system differ from the conductivity isotherms of the $ICl - AlCl_3 - C_6H_5NO_2$ system [2], where no such phenomenon was observed, although the conductivities of both these systems are of the same order of magnitude (10^{-3} mho).

Table 4

Specific Conductivity of the IBr – $AlBr_3$ – $C_6H_5NO_2$ System

Weight of $C_6H_5NO_2$, g	Weight of IBr, g	Weight of $AlBr_3$, g	IBr:$AlBr_3$ Molecular ratio	$\varkappa \cdot 10^3$
Series I: IBr:$C_6H_5NO_2$ Molar Ratio = 1:7.26				
7.4453	1.7254	–		0.99
7.4453	1.7254	0.0835	1:0.038	1.66
7.4453	1.7254	0.2054	1:0.092	2.64
7.4453	1.7254	0.7357	1:0.331	3.08
7.4453	1.7254	1.3999	1:0.629	3.18
7.4453	1.7254	1.8381	1:0.826	3.08
7.4453	1.7254	2.9845	1:1.341	2.32
7.4453	1.7254	4.7414	1:2.131	1.16
7.4453	1.7254	5.5914	1:2.513	0.88
7.4453	1.7254	6.2642	1:2.815	0.55
7.4453	1.7254	7.5763	1:3.405	0.21
Series II: IBr:$C_6H_5NO_2$ Molar Ratio = 1:25.03				
15.3771	1.0328	–	–	0.39
15.3771	1.0328	0.1116	1:0.084	0.57
15.3771	1.0328	0.1883	1:0.141	0.67
15.3771	1.0328	0.5452	1:0.492	1.10
15.3771	1.0328	0.9243	1:0.694	1.52
15.3771	1.0328	1.6970	1:1.274	2.03
15.3771	1.0328	2.7664	1:2.077	2.44
15.3771	1.0328	3.6399	1:2.733	2.49
15.3771	1.0328	5.0006	1:3.750	2.38

b) Cryoscopic Research on the IBr – $AlBr_3$ – $C_6H_5NO_2$ System

As is seen in Table 6, investigation of this system by the cryoscopic method indicated that adding aluminum bromide to a nitrobenzene solution of iodine bromide made the depression for the ternary system (Δt_3°) much less than the additive value obtained from the experimentally measured depressions: Δt_1° for the IBr – $C_6H_5NO_2$ system, and Δt_2° for the $AlBr_3$ – $C_6H_5NO_2$ system, at the respective concentrations of these bromides.

The cryoscopic determinations of the nitrobenzene solution of aluminum bromide were made for low concentrations of $AlBr_3$ (Table 5).

Table 5

Cryoscopy of the $AlBr_3$ – $C_6H_5NO_2$ System

Weight of $C_6H_5NO_2$, g	Weight of $AlBr_3$, g	$AlBr_3$:$C_6H_5NO_2$ molar ratio	$\Delta t°$	Molecular wt. of $AlBr_3$
17.5084	0.0223	1:17.02	0.032	272.58
17.5084	0.8273	1:45.89	1.175	275.46
11.1689	0.9718	1:24.91	2.176	273.76*
13.0090	2.2382	1:12.60	4.304	273.69*

The data for high $AlBr_3$ concentrations were taken from the paper by Mezhenny and Turov [6].

The depression Δt_2° for the concentrations of $AlBr_3$ given in Table 6 were

*Figures from Mezhenny and Turov [6].

determined from the data of Table 5 plotted graphically

Table 6

Cryoscopy of the IBr – $AlBr_3$ – $C_6H_5NO_2$ System

IBr:$C_6H_5NO_2$ Molar Ratio = 1:31.77

Test No.	Weight of $C_6H_5NO_2$ g	Weight of IBr, g	Δt_1°	Weight of $AlBr_3$, g	IBr:$AlBr_3$ / $C_6H_5NO_2$ molar ratio	$AlBr_3$ / $C_6H_5NO_2$ molar ratio	Δt_2°	$\Delta t_1^\circ + \Delta t_2^\circ$	Δt_3°	Δt_m°
1	17.8089	0.9423	1.73	0.0662	1:0.054	1:583.3	0.13	1.86	1.53	0.33
2	17.8089	0.9423	1.73	0.2071	1:0.170	1:186.4	0.32	2.05	1.30	0.75
3	17.8089	0.9423	1.73	0.3760	1:0.309	1:102.7	0.56	2.29	1.43	0.86
4	17.8089	0.9423	1.73	0.6226	1:0.512	1:62.02	0.91	2.64	1.69	0.95
5	17.8089	0.9423	1.73	0.8868	1:0.730	1:43.54	1.38	3.11	2.00	1.11
6	21.5237	1.6461	2.05	1.6515	1:0.778	1:23.38	2.36	4.41	3.30	1.11
					21.98					

The diminished depression for the ternary system, compared with the additive value, points to a reduction in the aggregate number of particles due to the formation of a coordination compound. It may also be assumed that the complex molecules formed in the solution undergo association.

This conclusion may also be drawn from the fact that the difference $[(\Delta t_1 + \Delta t_2) - \Delta t_3]$ rises with a rise in the $AlBr_3$:IBr ratio, as shown in the last column of Table 6.

Similar facts are likewise observed in the cryoscopy of the ICl – $AlCl_3$ – $C_6H_5NO_2$ system; in this system, however, the difference between the additive depression and that found experimentally was not as great as that in the IBr – $AlBr_3$ – $C_6H_5NO_2$ system. Evidently, the coordination compound formed in the latter system is more stable and possesses a much higher tendency toward association.

Study of Ion Transfer in the IBr – $AlBr_3$ – $C_6H_5NO_2$ System

Both qualitative electrolysis experiments and the quantitative nature of ion transfer in this system demonstrate complete similarity with the ICl – $AlCl_3$ – $C_6H_5NO_2$ system, in both systems the aluminum being transferred from the cathode area to the anode area [3].

In the electrolysis of this system it was found that solid iodine is deposited at the cathode, gradually dissolving as the experiment is prolonged.

As the electrolysis tests indicated, the best results are obtained in the study of ion transfer when electrolysis is carried out for a long time at low current strengths.

At high currents, the nitrobenzene may be resinified at one of the electrodes.

As is seen in Table 7, the percentage of aluminum in the cathode area diminishes owing to its transfer to the anode area as part of the complex anion.

A considerable increase in the percentage of bromine, transferred with the complex anion, is likewise observed in the anode area.

Δt_1°, found experimentally, is the depression for the IBr-$C_6H_5NO_2$ system; Δt_2° is the depression determined for the nitrobenzene solution of $AlBr_3$ at the given concentration; Δt_3° is the depression found experimentally for the IBr-$AlBr_3$-$C_6H_5NO_2$ system, and Δt_m° is the difference between the depression computed by the additivity principle and that found experimentally for the ternary system, i.e. $[(\Delta t_1 + \Delta t_2) - \Delta t_3]$.

Table 7

Ion Transfer in the $IBr - AlBr_3 - C_6H_5NO_2$ System

Test No.	Composition of the tested solution $\frac{IBr:AlBr_3}{C_6H_5NO_2}$	Cu deposited in the coulomb meter, g	substance measured	Solution after Electrolysis: cathode portion, expected reading g	cathode portion, found g	cathode portion, Δg	middle portion, expected reading, g	middle portion, found g	middle portion, Δ g	anode portion, expected reading g	anode portion, found g	anode portion, Δ g
1	$\frac{1:0.553}{7.564}$	0.1042	Al	0.0893	0.0794	-0.0099	0.0639	0.0633	-0.0006	0.1017	0.1116	+0.0099
			I	0.7604	0.5158	-0.2446	0.5438	0.5430	-0.0008	0.8661	1.1100	+0.2439
			Br	1.2730	0.6118	-0.6612	0.9103	0.9109	+0.0006	1.4500	2.1 24	+0.6724
2	$\frac{1:0.314}{10.162}$	0.0446	Al	0.0447	0.0407	-0.0040	0.0177	0.0175	-0.0002	0.0464	0.0503	+0.0039
			I	0.6698	0.5182	-0.1516	0.2651	0.2644	-0.0007	0.6959	0.8567	+0.1608
			Br	0.8192	0.5546	-0.2846	0.3242	0.3002	-0.0040	0.8511	1.1396	+0.2885
3	$\frac{1:0.591}{8.053}$	0.1013	Al	0.1111	0.1021	-0.0090	0.0623	0.0614	-0.0009	0.1138	0.1227	+0.0089
			I	0.8848	0.6229	-0.2619	0.4967	0.4960	-0.0007	0.9066	1.1740	+0.2674
			Br	1.5450	0.8091	-0.7359	0.8657	0.8663	+0.0006	1.5831	2.3184	+0.7353
4	$\frac{1:0.585}{7.653}$	0.0875	Al	0.0790	0.0703	-0.0087	0.0507	0.0508	+0.0001	0 0829	0.0915	+0.0086
			I	0.7669	0.5345	-0.2324	0.4916	0.4913	-0.0003	0.8061	1.0576	+0.2525
			Br	1.1554	0.6037	-0.5817	0.7594	0.8325	+0.0731	1.2443	1.7518	+0.5075

A certain increase in the iodine percentage in the anode area may be due to side (secondary) processes taking place during electrolysis.

The results obtained in our investigation of the

$$IBr - AlBr_3 - C_6H_5NO_2$$

system agree with the results of investigation of the

$$ICl - AlCl_3 - C_6H_5NO_2$$

system. Hence, the conclusions concerning the nature of the electrolyte formed in these systems are wholly similar and reinforce each other.

The higher conductivity and smaller depression of the $IBr - AlBr_3 - C_6H_5NO_2$ system (as against the properties of a solution of IBr in nitrobenzene) point to a process of coordination-compound formation.

The phenomena observed in our study of ion transfer in the $IBr - AlBr_3 - C_6H_5NO_2$ system justify the conclusion that aluminum and bromine are part of the anion of the coordination compound formed in that solution. It likewise follows from the electrolysis experiments that the cation of this coordination compound

This conclusion is not contradicted by the fact that electrolysis results in an increase of the iodine percentage in the anode area.

When the positively charged iodine ions are discharged at the cathode, free (molecular) iodine is formed at first. As we know from the work of Brunner

and Galecki [7], when a nitrobenzene solution of iodine is electrolyzed, the latter moves to the anode. This may be due to the fact that a coordination compound of nitrobenzene and iodine, $C_6H_5NO_2 \cdot I_2$ in the simplest case, undergoes electrolysis.

We may assign the structure $[C_6H_5NO_2 \cdot I]I$ to this coordination compound on the basis of the theoretical considerations set forth in our previous communications [2,3], in accordance with which part of the iodine should move into the anolyte during electrolysis.

This sort of phenomenon should also exist in the system investigated by us.

Measurement of the viscosity of the $IBr - AlBr_3$ system indicated the formation of a coordination compound $IBr \cdot AlBr_3$ [1]. If it is assumed that a coordination compound of this sort persists in the nitrobenzene solution, it must be assigned the structure $I[AlBr_4]$, on the basis of the experiments described above. Then the electrolytic dissociation of this coordination compound and the processes taking place during electrolysis may be represented by the following equations:

$$I[AlBr_4] \rightleftharpoons I^+ + [AlBr_4]^- ;$$

$$2I^+ + 2\underline{e} = I_2;$$

$$2[AlBr_4]^- - 2\underline{e} = 2AlBR_3 + BR_2.$$

The fact that iodine is transferred to the anolyte due to secondary processes is evident from the circumstance that the number of equivalents of transferred iodine is much lower than the number of equivalents of bromine transferred to the anolyte in the very same experiment.

SUMMARY

1. Investigation of the $IBr - KBr - C_6H_5NO_2$ and $IBr - AlBr_3 - C_6H_5NO_2$ systems indicates that potassium bromide and aluminum bromide form coordination compounds with iodine bromide in a nitrobenzene solution that are identical in nature with the compounds of iodine chloride with potassium or aluminum chloride.

2. The results of electrolysis and ion-transfer tests of the $IBr - KBr - C_6H_5NO_2$ and $IBr - AlBr_3 - C_6H_5NO_2$ systems show that the coordination compound of KBr with iodine bromide has the structure of $K[IBr]_2$, whereas the coordination compound of $AlBr_3$ and iodine bromide must be assigned the structure of $I[AlBr_4]$.

3. Hence, the results obtained confirm that compounds of IBr with KBr or $AlBr_3$, like the compounds of ICl with KCl or $AlCl_3$, cannot be considered polyhalides; they must be looked upon as binary halides (halogen salts).

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THE SOLUBILITY OF SILVER BROMATE IN ELECTROLYTE SOLUTIONS

I. $AgBrO_3$-NITRATE OF AN ALKALINE-EARTH METAL-WATER SYSTEM

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It is generally recdgnized at the present time that the solubility of poorly soluble substances (precipitates) is affected not only by similar ions of other salts, but also by any other ions as well. This circumstance sets a certain limit to the feasibility of employing calculations based upon acceptance of the rule of constancy of the solubility product, with allowance made solely for the influence of like ions (Nernst, Noyes).

The well-known formula of Debye and Hückel, in which the effect of the medium upon the solubility of the precipitate is governed by the magnitude of the electrolyte's coefficient of activity, depending upon the ion ionic strength of the solution, appears much more widely accepted. The new viewpoint, whose general validity made it inviting, attracted the attention of new research workers, thus giving rise to a fairly extensive literature, as reflected, in particular, in the papers by A.F.Kapustinsky [1] and I.V.Tananayev and I.B.Mizetskaya [2].

The principal factor in the new theory is the feasibility of allowing for the effect of other salts upon the solubility of the precipitate, having as its basis the individual nature of salt ions. The latter is achieved by introducing supplementary constants into the formulas, which eliminate the first-approximation defect of the Debye-Hückel formula. The question of the extent to which these constants can be predicted from the known physical characteristics of the ions (chiefly the ionic radius) remains an open one, as only comparatively little precise research has been done up to now to provide enough computed and experimental data for comparison, thus determining the actual value of thecorresponding formulas. The paper that has been most widely used in this respect is the cited paper by I.V.Tananayev and I.B.Mizetskaya, who investigated the solubility of $PbSO_4$ in solutions of lithium, sodium, potassium, calcium, aluminum, and lead nitrates, and of hydrogen, lithium, sodium, and potassium sulfates. The authors established a regularity of behavior for $PbSO_4$, consisting of an apparently general tendency for the ions to increase the solubility of this precipitate as the ion radius decreases in the given group (K → Li; Ba → → Mg) and in the given row (from left to right) of the Periodic Table. The extent to which this assertion holds true for other systems is as yet uncertain, and research in this field must be recognized as extremely important to analytical chemistry.

The work of Soviet scientists in this field is characterized by the scale upon which the problem has been posed, as expressed in the employment of the methods of physico-chemical analysis developed by the school of N.S.Kurnakov. This research program in precipitate solubility should cover the broad (practicably realizable) range of concentrations of alien electrolytes as well as, where possible, a large number of the electrolytes themselves. Only in such an approach to the study of precipitate solubility can we expect sufficiently broad generalizations in which both physical and chemical factors will play their part.

It should be noted that the investigation of such systems (precipitate – electrolyte with like ions – water) only partly solves the problems from the standpoint of practical chemical analysis, inasmuch as actual operating systems are four-component systems (the usual exchange reactions with deposition of a precipitate). This is why ternary systems should be studied only within the framework of a general approach to the problem, involving research into systems with a large number of actually active components.

The present paper is the first communication of a series devoted to research into the solubility of silver bromate in solutions of various electrolytes, both containing as well as not containing common ions.

The goal of the research as a whole is the study of the laws applying to ternary and corresponding quaternary systems with ions (cations and anions) of different valency (from unity to four). Silver bromate was chosen as the precipitate because it is a model of an electrolyte with one-to-one valency whose solubility is not too low. It was presumed that a precipitate of this ionic type would be an example of the most ideal behavior of a slightly soluble salt in systems with extraneous electrolytes, with collateral phenomena (such as the formation of intermediate and coordination compounds) due to the presence of multivalent ions in the precipitate reduced to a minimum. Moreover, silver bromate is the first of a series of precipitates that are to be investigated in the future.

Initial Substances and Methods of Work

The difficulty of preparing pure $AgBrO_3$ is noted in the literature [3], the bromates of the alkali metals occurring in the precipitate as the result of the formation of solid solutions being mentioned as the impurities involved. The following method of operation was adopted to eliminate this.

An equivalent quantity of a 5% solution of $KbRO_3$ was added drop by drop in the cold to a 10% solution of $AgNO_3$, with constant motor-driven stirring. After repeated washings the precipitate was recrystallized, washed with double-distilled water, squeezed out on the filter paper, and air-dried. The preparation was kept in a dark glass jar. All the salts employed as extraneous electrolytes were recrystallized twice, no matter what their origin. The solutions required were prepared by suitably diluting standard molar solutions, with carefully established titers.

Double-distilled water, kept in vessels paraffined on the inside, was used in preparing and diluting the solutions.

The experiments to determine the solubility of $AgBrO_3$ were made in 400-ml paraffined bottles of brown glass. The stoppered bottle (with an opening in the stopper for the stirrer), containing 1 g of $AgBrO_3$ in the given medium, was placed in a thermostat at a temperature of 25 $\pm$0.1°, the solution was energetically stirred by the motor-driven stirrer for 6 to 8 hours.

The solution (250 ml) with the precipitate was left in the thermostat for 1 to 1.5 hours before being taken out for analysis. The concentration of the dissolved $AgBrO_3$ was determined by the percentage of silver in the saturated solution (determined by weight as AgCl). All operations were performed in beakers shielded against light by black paper.

Two parallel tests were run for each point, and two analyses were made each test. The mean value was taken as the $AgBrO_3$ solubility.

Solubility of $AgBrO_3$ in Water

The mean value of the solubility of $AgBrO_3$ in water at 25°, as found by us, is 0.1948 g per 100 ml. As may be seen from Table 1, our figure is closest to those

of Hill and Reedy, which seemed to us to be most reliable. The value of $AgBrO_3$ solubility found by us ($8.26 \cdot 10^{-3}$ mole per liter) was taken as a basis for all later computations.

TABLE 1

Comparative Data on the Solubility of $AgBrO_3$ in Water

Author and year	t°	$AgBrO_3$ solubility, %
Longi, 1883 [4]	25	0.166
Noyes, 1890 [5]	24.5	0.192
Böttger, 1903 [6]	25	0.159
Whitely, 1910 [7]	27	0.171
Hill, 1917 [8]	25	0.195
Reedy, 1921 [9]	25	0.196
Dalton and assoc., 1924 [10]	25	0.189 – 0.191
Owen, 1933 [11]	25	0.192
Neuman, 1934 [12]	25	0.192
Ricci and Aleshnik, 1944 [3]	25	0.204 ± 0.004
Tananayev, Lelchuk, and Petrovitskaya	25	0.195

Solubility Data of $AgBrO_3 - Me(NO_3)_2 - H_2O$ Systems, where Me = Mg, Ca, Sr, and Ba

The results of solubility determinations performed by the method described above are listed in Tables 2, 3, 4 and 5. The first column of these tables shows the concentration of the nitrate of the alkaline-earth metal; the second column gives the molarity of $AgBrO_3$ in the saturated solution; the third column gives the ionic strength of the solution; the fourth column gives the activity coefficient of $AgBrO_3$; the fifth column gives the ion product of $AgBrO_3$; and the sixth column gives the activity product of $AgBrO_3$.

The activity coefficient of $AgBrO_3$ (fourth column) was computed by a method elaborated by I.V.Tananayev and I.B.Mizetskaya [2]. Starting with the assumption that the activity product of $AgBrO_3$ is constant, taken as:

$$(Ag^{\cdot}) \cdot (BrO_3^{\prime}) \cdot \gamma^2 = Lp_{AgBrO_3} \cdot \gamma^2 = La_{AgBrO_3}, \qquad (1)$$

the activity coefficient was computed for each experiment from the following formula:

$$\gamma = \sqrt{\frac{La}{Lp}}, \qquad (2)$$

as the quantities La and Lp were known for $AgBrO_3$. Then the quantity a was computed from the formula:

$$-\log \gamma = \frac{0.505\sqrt{\mu}}{1 + 0.33 \cdot a\sqrt{\mu}} \qquad (3)$$

by substitution. As I.V.Tananayev and I.B.Mizetskaya discovered, this computation should be made for solutions with high concentrations of extraneous salts, when a varies considerably with concentration. In our example, the value of a was found for the highest concentration of $Me(NO_3)_2$ (1 mole per liter; 0.3 mole per liter for $Ba(NO_3)_2$). Then γ_{AgBrO_3} was computed by substituting this value of a in Equation (3), after which La is computed from Equation (1). The values of a obtained in this fashion are listed in Column 7.

TABLE 2

Solubility of $AgBrO_3$ in $Mg(NO_3)_2$ Solutions

$Mg(NO_3)_2$, moles per liter	$AgBrO_3$ moles per liter	μ	γ	Lp	La	a
0.000	0.00826	0.00826	0.900	$6.83 \cdot 10^{-5}$	$5.5 \cdot 10^{-5}$	
0.001	0.00856	0.0116	0.891	$7.33 \cdot 10^{-5}$	$5.82 \cdot 10^{-5}$	
0.003	0.00872	0.0177	0.870	$7.60 \cdot 10^{-5}$	$5.75 \cdot 10^{-5}$	
0.01	0.00928	0.0393	0.820	$8.61 \cdot 10^{-5}$	$5.78 \cdot 10^{-5}$	2.41
0.03	0.00981	0.100	0.746	$9.62 \cdot 10^{-5}$	$5.36 \cdot 10^{-5}$	
0.1	0.0111	0.302	0.634	$1.23 \cdot 10^{-4}$	$4.95 \cdot 10^{-5}$	
0.3	0.0127	0.913	0.532	$1.61 \cdot 10^{-4}$	$4.56 \cdot 10^{-5}$	
1.0	0.0173	3.017	0.428	$3.00 \cdot 10^{-4}$	$5.5 \cdot 10^{-5}$	

TABLE 3

Solubility of $AgBrO_3$ in $Ca(NO_3)_2$ Solutions

$Ca(NO_3)_2$ Moles per liter	$AgBrO_3$ moles per liter	μ	γ	$Lp \cdot 10^5$	$La \cdot 10^5$	a
0.000	0.00826	0.00826	0.900	6.83	5.50	
0.001	0.00791	0.0109	0.893	6.26	4.99	
0.003	0.00807	0.0171	0.870	6.51	4.93	
0.01	0.00915	0.0392	0.818	8.36	5.58	2.19
0.03	0.00988	0.100	0.741	9.74	5.35	
0.01	0.0111	0.311	0.630	12.3	4.88	
0.3	0.0133	0.913	0.519	17.7	4.77	
1.0	0.0181	3.018	0.410	32.8	5.50	

TABLE 4

Solubility of $AgBrO_3$ in $Sr(NO_3)_2$ Solutions

$Sr(NO_3)_2$, moles per liter	$AgBrO_3$ moles per liter	μ	γ	$Lp \cdot 10^5$	$La \cdot 10^5$	a
0.000	0.00826	0.00826	0.900	6.83	5.50	
0.001	0.00840	0.0114	0.890	7.06	5.60	
0.003	0.00859	0.0176	0.867	7.38	5.55	
0.01	0.00896	0.0390	0.815	8.03	5.34	1.92
0.03	0.0100	0.100	0.736	10.0	5.41	
0.1	0.0122	0.312	0.605	14.9	5.45	
0.3	0.0143	0.914	0.500	20.4	5.10	
1.0	0.0194	3.019	0.382	37.6	5.50	

As for the initial value of La_{AgBrO_3}, it is found from Equation (1), the activity coefficiant required for this being computed from the following formula:

$$-\log\gamma = 0.505\ \sqrt{\mu}$$

since the coefficient a may be ignored for dilutions corresponding to an aqueous solution of $AgBrO_3$.

TABLE 5

Solubility of $AgBrO_3$ in $Ba(NO_3)_2$ Solutions

$Ba(NO_3)_2$ moles per liter	$AgBrO_3$ moles per liter	μ	γ	$Lp \cdot 10^5$	$La \cdot 10^5$	à
0.000	0.00826	0.00826	0.900	6.83	5.50	
0.001	0.00824	0.0112	0.891	6.78	5.38	
0.003	0.00839	0.0174	0.868	7.04	5.30	
0.01	0.00894	0.0389	0.816	8.00	5.31	1.91
0.03	0.00991	0.100	0.736	9.82	5.31	
0.01	0.0122	0.312	0.619	1.48	5.67	
0.3	0.0149	0.915	0.498	2.22	5.50	

Evaluation of Results

As is seen from the foregoing tables and the corresponding curves (Figs. 1, 2, 3, and 4), the behavior of $AgBrNO_3$ is characteristic for all the systems. The solubility of $AgBrO_3$ in solutions of all the alkaline-earth nitrates regularly increases with increasing concentrations of the latter, compared to its solubility in water. Correspondingly, Lp_{AgBrO_3} likewise rises steadily, this rise being much more marked at high concentrations of $Me(NO_3)_2$.

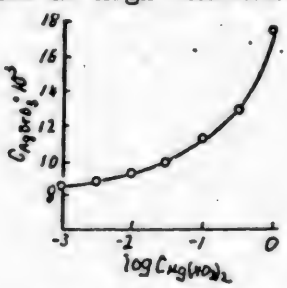

Fig. 1. Solubility of $AgBrO_3$ in $Mg(NO_3)_2$ solutions.

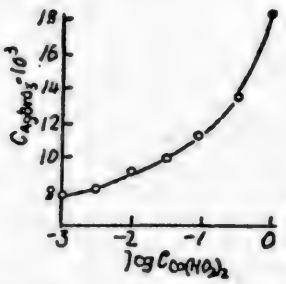

Fig. 2. Solubility of $AgBrO_3$ in $Ca(NO_3)_2$ solutions

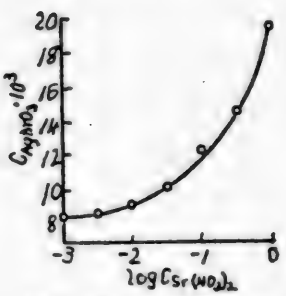

Fig. 3. Solubility of $AgBrO_3$ in $Sr(NO_3)_2$ solutions.

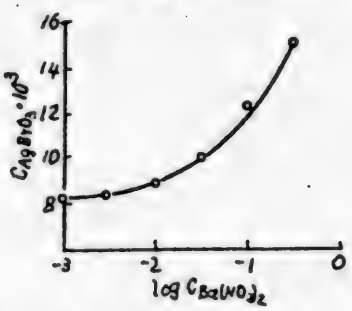

Fig. 4. Solubility of $AgBrO_3$ in $Ba(NO_3)_2$ solutions.

This is strikingly illustrated in the figures of Table 6 and in Fig. 5, in which the curves showing the variation of Lp_{AgBrO_3} in solutions of the nitrates of all the four alkaline-earth metals are plotted. As we see, the curves are clearly distinct from one another only at $Me(NO_3)_2$ concentrations that are higher than 0.1

mole per liter; below this concentration the influence of the nitrate cation is practically negligible.

TABLE 6

Variation of Lp_{AgBrO_3} in $Me(NO_3)_2$ Solutions

$C_{Me(NO_3)_2}$ mol/l	log $C_{Me(NO_3)_2}$	$Mg(NO_3)_2$		$Ca(NO_3)_2$		$Sr(NO_3)_2$		$Ba(NO_3)_2$	
		$Lp \cdot 10^5$	log Lp	$Lp \cdot 10^5$	log Lp	$Lp \cdot 10^5$	log Lp	$Lp \cdot 10^5$	log Lp
0.001	-3.0	7.33	-4.14	6.26	-4.2	7.06	-4.15	6.78	-4.17
0.003	-2.5	7.60	-4.12	6.51	-4.19	7.38	-4.13	7.04	-4.15
0.01	-2.0	8.61	-4.07	8.36	-4.1	8.03	-4.1	8.0	-4.1
0.03	-1.5	9.62	-4.02	9.74	-4.0	10.0	-4.0	9.82	-4.0
0.1	-1.0	12.3	-3.91	12.3	-3.9	14.9	-3.83	14.8	-3.83
0.3	-0.5	16.1	-3.79	17.7	-3.77	20.4	-3.69	22.2	-3.65
1	±0.0	29.9	-3.52	32.8	-3.48	37.6	-3.42	–	–

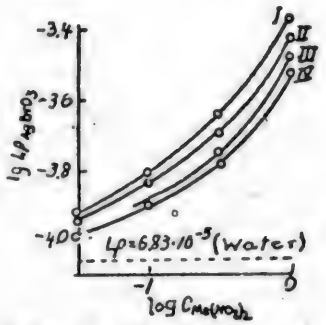

Fig. 5. Variation of Lp_{AgBrO_3} in $Me(NO_3)_2$ solutions.

I-$Ba(NO_3)_2$; II-$Sr(NO_3)_2$; III-$Ca(NO_3)_2$; IV-$Mg(NO_3)_2$.

These cations fall into the following series in the order of their increasing influence on the solubility of $AgBrO_3$:

$$Mg < Ca < Sr < Ba.$$

The value of a that ensures a constant value for La varies inversely (that is, diminishes) from 2.4 to 1.8 from magnesium to barium. The latter figure for $Ba(NO_3)_2$ was found by extrapolation, owing to the limited solubility of this salt.

It is worthy of note that the value of a, which plays so important a part, is largely governed by the concentration of the electrolyte. The nature of the variation of a is seen in Table 7, where the variation of a in 0.3 molar and molar solutions of $Me(NO_3)_2$, is shown.

Though the value of a continues to drop (from magnesium to barium), its absolute value exhibits noticeable differences. As the concentration of $Me(NO_3)_2$ drops, the relative difference in the values of a increases for the various elements. Thus, for molar solutions of $Me(NO_3)_2$, a takes on an extreme value: 2.41 for $Mg(NO_3)_2$ and 1.80 for $Ba(NO_3)_2$, whereas a varies between the limits of 3.37 and 1.90, respectively for 0.3 molar solutions. We thus note a tendency for the a values of different cations to approach one another as the electrolyte concentration is increased.

TABLE 7

Behavior of $AgBnO_3$ in 0.3 Molar and 1 Molar Solutions of $Me(NO_3)_2$

Electrolyte	$C_{AgBrO_3} \cdot 10^2$		$Lp':Lp$*		a	
	$Me(NO_3)_2$ 0.3 moles/l	$Me(NO_3)_2$ 1 mole/l	$Me(NO_3)_2$ 0.3 moles/l	$Me(NO_3)_2$ 1 mole/l	$Me(NO_3)_2$ 0.3 moles/l	$Me(NO_3)_2$ 1 mole/l
$Mg(NO_3)_2$	1.27	1.73	2.36	4.37	3.37	2.41
$Ca(NO_3)_2$	1.33	1.81	2.59	4.80	2.84	2.19
$Sr(NO_3)_2$	1.43	1.84	2.99	5.50	2.17	1.92
$Ba(NO_3)_2$	1.49	–	3.25	–	1.90	1.80 **

* Lp' and Lp a e the ion products of $AgBrO_3$ in salt and water solutions, respectively.

** Found by extrapolation (Fig. 6).

This phenomenon may, moreover, be considered in the light of the definite requirements concerning the agreement of the computed value of La with the experimental data.

As may be seen in Tables 2, 3, 4, and 5, La, is not a constant in the strict sense of the term, but varies, reaching something of a minimum in the region where the values of $C_{Me(NO_3)_2}$ are from 0.3 to 0.1 moles per liter.

The resulting curvature of the respective curves gradually decreases from magnesium to strontium, vanishing entirely for barium. As I.V.Tananayev and I.B.Mizetskaya [2] have shown, in such cases La may be held rigidly constant by introducing another term, H into the computational formula. In the present paper, however, we do not think it necessary to do this, assuming that discrepancies as high as 20% in the value of Lp (say, in the case of $Mg(NO_3)_2$) are allowable in reaching conclusions as to the behavior of the precipitate under the conditions of analytical practice. This assumption simplifies the whole system of calculations considerably.

The greatest increase in Lp_{AgBrO_3} (5.5 times) is observed in the molar solution of $Sr(NO_3)_2$. In a $Ba(NO_3)_2$ solution of the same concentration, Lp_{AgBrO_3} would probably rise still higher. This increase is relatively small, but it should be borne in mind that as the solubility of the precipitate diminishes, Lp increases much more (hundreds and even thousands of times) under similar conditions.

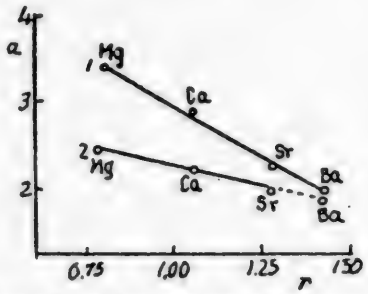

Fig. 6 Value of a as a function of the ionic radius of the $Me(NO_3)_2$ cation.

It was the goal of the present paper to determine the character of the relationship between the nature of the cation and its influence upon the solubility of relatively insoluble salts. From this standpoint the greatest interest attaches to consideration of the variation of a with the magnitude of the ionic radius of the cation of the extraneous salt (for the same anion). As is seen in Fig. 6, where a is plotted against the ionic radii (r) of various cations, the values of a lie along a straight line, thus testifying to the existence of an obvious relationship between a and the ionic radius. The positions of the curves also indicate the nature of the variation of a with the concentration of the electrolyte, which differs for various cations and is more markedly evident the smaller the ionic radius.

Table 8 and Fig. 7 illustrate the variation of the precipitate's γ in the solution as a function of the concentration of the alkaline-earth metal's nitrate. The mean values of γ_{AgBrO_3} found for the various electrolytes were used in plotting the curve. Notwithstanding the fact that these values diverge noticeably at concentrations above 0.1 mole per liter, they characterize the behavior of $AgBrO_3$ at the given ionic strength of the solution fairly well. As we see, γ_{AgBrO_3} drops to 0.4 for an ionic strength of 3. It is quite natural that computation using Lp cannot yield correct results, since this involves a unity value for γ.

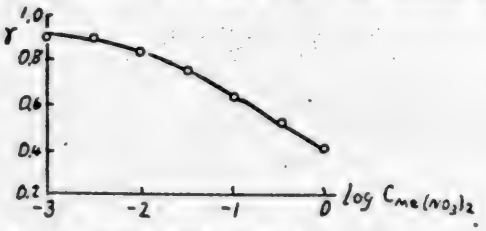

Fig. 7. Mean value of γ_{AgBrO_3} as a function of $C_{Me(NO_3)_2}$.

It follows from the foregoing that the solubility of $AgBrO_3$ should be calculated from the following formula, using data of its solubility in solutions of the nitrates of alkaline-earth elements:

$$C_{AgBrO_3} = \sqrt{\frac{La}{\gamma^2}},$$

where La = $5.5 \cdot 10^{-5}$, and γ is found by means of the curve of Fig. 7.

TABLE 8

Summary of γ_{AgBrO_3} Data in $Me(NO_3)_2$ Solutions of Various Concentrations

$C_{Me(NO_3)_2}$	γ_{AgBrO_3} in Solutions of				Mean value of γ_{AgBrO_3}
	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$	
0.000	0.900	0.900	0.900	0.900	0.900
0.001	0.891	0.893	0.890	0.891	0.891
0.003	0.870	0.870	0.867	0.868	0.869
0.01	0.820	0.818	0.815	0.816	0.817
0.03	0.746	0.741	0.736	0.736	0.740
0.1	0.634	0.630	0.619	0.619	0.625
0.3	0.532	0.519	0.500	0.498	0.513
1.0	0.428	0.410	0.382	–	0.407

The value of γ can also be computed for the given ionic strength, which is assumed to be known (based, say, on measurement of the aggregate electrical conductivity of the solution), by means of the following formula:

$$-\log\gamma = \frac{0.505 \cdot \sqrt{\mu}}{1 + 0.33 \cdot a \cdot \sqrt{\mu}},$$

in which the value of a may be taken as the mean of the values found above for each of the four cations.

According to the data of Table 7 (last column), the mean value of a is 2.1 for molar solutions of $Me(NO_3)_2$. To be sure, the values found will not be very accurate with this sort of approach, but it should be remembered that, on the basis of the ion-product rule, computation of precipitate solubility is altogether impossible in such cases (i.e., when like ions are absent).

In our next report, we shall show how these observed patterns of behavior are generally applicable to other salts, particularly to the nitrates of alkali metals and metals of high valency.

SUMMARY

The solubility of $AgBrO_3$ in solutions of magnesium, calcium, strontium, and barium nitrates was investigated for salt concentrations up to 1 mole per liter, at 25°.

The experimental data were used to calculate the value for a, by means of the second variant of the Debye-Hückel formula. Then the value of the activity coefficient (γ) of $AgBrO_3$ was computed on the assumption that the La, (the activity product) of $AgBrO_3$, which was found to be $5.5 \cdot 10^{-5}$, was constant. The scale of variation of Lp_{AgBrO_3} as a function of the solution's ionic strength is shown, and formulas are proposed for computing the solubility of $AgBrO_3$ from the La_{AgBrO_3}.

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BINARY LIQUID SYSTEMS CONTAINING ACETIC ACID

I. THE ELECTRICAL CONDUCTIVITY OF THE ACETIC ACID-ANALINE SYSTEM

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It is known that the presence of an associated component in a system introduces a number of complications in the latter's behavior when its composition is changed. These complications are manifested in departures from the regular behavior patterns established for systems containing normal, nonassociated components. This results in considerable difficulty in interpreting composition – property diagrams, especially of irrational systems, often making it impossible to reach definite conclusions regarding the interrelationship of the system's components.

In reviewing the results of research on systems between whose components chemical interaction is possible and one of whose components is associated, we usually find two processes simultaneously going on within the system: the breakdown of the associated molecules into simple ones, on the one hand, and chemical interaction of the system components on the other. Depending upon which of these processes exerts a greater effect upon the system's behavior, we get different diagrams, whose appearance either confirms the presence of chemical interaction, established in the study of other properties, or contradicts it.

It must be supposed that the competition between these two processes will be extremely marked in systems with components that are very firmly associated and whose polymeric molecules cannot interact any further. A substance of this sort can take part in reactions only as its simple molecules. The decomposition of polymers and, hence, the chemical interaction of substances of this sort will take place more or less readily only when the system components have sharply different chemical functions, i.e., one of them acts as an acid, while the other behaves like a base in the sense of Brönsted's theory [1]. In such systems chemical action should be rather clearly reflected in the composition – property diagram.

The picture observed for systems consisting of normal (nonassociated) components may be distorted considerably for systems with associated components if the difference between the chemical functions of the components is slight and chemical interaction occurs between them, accompanied by the formation of unstable coordination compounds. The degree of molecule association is high in systems of this sort, which is why polymeric molecules must be present in all component relationships. The existence of the latter molecules must, in our opinion, be borne in mind in computing the molecular percentage of associated components in the system. Otherwise, i.e., when the usual calculation using only simple molecules, is employed, the "singular" points on the composition – property diagram may be displaced from the ordinate of the compound formed within the system.

Our research had as its object tracing the behavior of systems containing firmly associated components while two parallel processes were taking place simultaneously: the process of the breakdown of the associated molecules into simple ones, and the chemical interaction of these simple molecules with the molecules of the other component when an acid-basic function is manifested.

All the systems investigated contained acetic acid, the molecules of which are.

associated in dimers, as we know, which do not break down even when the acid is transformed into the gaseous state [2] and are incapable of further addition. Several organic bases (aniline, pyridine) and acids (HNO_3, $CH_2ClCOOH$) of different strengths were used as the second component. In combination with these components acetic acid ought to yield systems with chemical action of varying degree.

In our investigations we mostly used the method of studying electrical conductivity and its temperature coefficient, since, according to M. Usanovich [3,4], the diagram of the temperature coefficient of conductivity indicates the composition of the compounds formed of the system components.

The viscosity and density were also investigated for some of the systems.

Electrical Conductivity of $C_2H_4O_2 - C_6H_5NH_2$

This system has been investigated by many authors. At the time of our research we had data on the following of its properties: conductivity [5,6, 7,8,9,10,11], viscosity and density [12,13,14,21], melting point [15,16], refractive index [17,18], and magnetic rotation of the polarization plane [11].

The available data on the electrical conductivity of the $C_2H_4O - C_6H_5NH_2$ did not enable us to reach any definite conclusions concerning the nature of the interaction between its components or the quantity and composition of the compounds formed in the system. This may be due to the fact that the conductivity had been investigated either only at one temperature or incompletely, i.e., only for a few concentrations. Neither of these defects exists in the research done by Konovalov [5], but, as we know, the author's conclusions regarding the composition of the compounds formed within the system are questionable.

In order to track the effect of chemical action upon the curves of specific conductivity and its temperature coefficient, we investigated the conductivity in greater detail and at two temperatures. Moreover, we proposed to compare our data with the fairly extensive experimental data on other properties of the system in order to trace the effect of association upon the system's behavior and the reflection of this influence in the composition--property diagrams.

All previous research workers found chemical action to occur within the system, but only a few of them indicate, more or less precisely, the composition of the compounds newly formed in the system. It is conjectured, for example, that compounds of the following composition are formed:

$2C_2H_4O_2 \cdot C_6H_5NH_2$ [15, 16]; $2C_6H_5NH_2 \cdot C_2H_4O_2$ [15].

The latter compound is metastable, however, as the authors themselves indicate.

EXPERIMENTAL

The objects of our research were purified in the usual manner, namely: anhydrous acetic acid was purified by repeated fractional freezing (the last freezing was done in sealed ampoules). The purified acid had a m.p. of 16.6° and a specific conductivity of the order of $1 \cdot 10^{-7}$ mho. The aniline was desiccated, first with potassium hydroxide, and then with metallic sodium over which it was distilled. The fraction boiling at 182-183° was taken for our tests. Conductivity was measured by the usual Kohlrausch method.

The electrolysis volume of the vessels ranged from 0.3151 to 0.5951.

The conductivity of the acetic acid--aniline system was measured immediately after the solution had been prepared, since it changed with the passage of time.

After the acetic acid was mixed with the aniline, the mixture heated up considerably.

Conductivity was measured at 21 and 50°. The first isotherm was taken in order to be able to compare our data with those of Konovalov and of Trifonov and Cherbov; the other one was chosen arbitrarily in order to be able to compute the temperature coefficient of conductivity. The results of measurement are given in Table 1 and are shown graphically in Fig. 1 (circles) showing the specific conductivity (κ) as a function of the composition. This table also gives the values of the conductivity temperature coefficient (C) as calculated for the interval 21-50°.

TABLE 1

Molecular percent of $C_6H_5NH_2$	Specific conductivity, $\kappa \cdot 10^{-3}$		$C_{21-50} \cdot 10^{-2}$
	21°	50°	
6.48	2.107	3.906	2.944
10.30	2.451	4.916	3.468
17.29	2.645	6.349	4.829
21.41	2.613	6.717	5.416
25.72	2.474	6.654	5.826
27.90	2.354	—	—
32.02	2.232	5.934	5.719
30.75	2.195	5.874	5.780
33.63	2.361	6.261	5.709
39.00	2.413	5.807	4.860
41.97	2.344	5.206	4.210
47.90	1.952	3.667	3.030
53.33	1.574	2.449	1.902
63.18	0.871	0.873	0.00871
73.15	0.182	0.114	-1.281
73.53	0.197	0.121	-1.336
87.47	0.00605	0.0048	-0.704

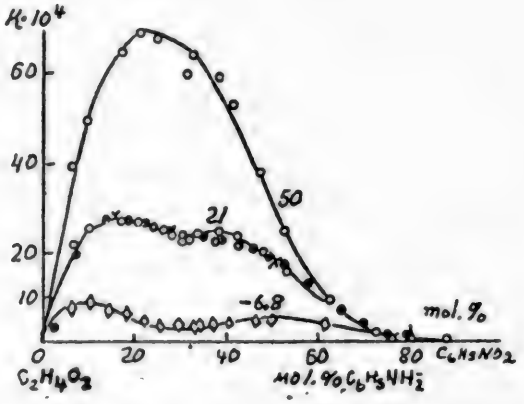

Fig. 1. Conductivity isotherms.

Figure 1 also gives the isotherms plotted by Konovalov (solid dots), Trifonov and Cherbov [11] (crosses), and Klochko and Chanukvadze [19] at the temperature of 6.8°, (diamonds). It is evident from Fig. 1 that the nature of the isotherm plotted by us fully conforms with those plotted by the foregoing authors, as well as with the data of M. Klochko and O. Chanukadze.*

The curve of specific conductivity plotted by us passes through a maximum, exhibiting a point of inflection at intermediate temperatures, as do the curves of the other research workers. We investigated the conductivity at concentrations corresponding to this point of inflection in greater detail than the preceding authors. Our point of inflection turned out to be more clearly defined and justified the assumption that a minimum would exist on the isotherms at lower temperatures. This latter hypothesis is corroborated by the research of Klochko and Chanukadze. The minimum is located at 33 mol % of aniline. As the temperature is raised, the point of inflection smooths out, finally vanishing entirely, while the location of the maximum is shifted. At 50°, maximum conductivity occurs at about 25 mol % of aniline. At -6.8°, the maximum is at 10.5 mol % of aniline.

Raising the temperature also increases the conductivity appreciably, as is seen in Fig. 2; this is due, no doubt to a decrease in the viscosity. Fig. 2 shows the magnitude of the conductivity temperature coefficient (C) as a function of the concentration. The figure also gives one of the curves for the temperature coefficient computed by Klochko and Chanukadze (diamonds). The location of the

*We learned of these results while we were writing up the present report.

maximum on the temperature-coefficient curves is at 33 mol % of aniline. It should be noted that the temperature coefficient of conductivity is negative for solutions containing a high percentage of acetic acid. This is probably due to the fact that the effect of the decomposition of the exothermic electrolyte upon the conductivity outweighs the contrary effect of the increase in ion mobility with temperature. In order to observe the behavior of the conductivity independently of the viscosity we eliminated the latter factor, multiplying over conductivity values (for 50°) by the corresponding values for the internal friction (Table 2) found by Klochko and Chanukadze. The "reduced" conductivity curve thus derived is shown in Fig. 3.

TABLE 2

Molecular % of $C_6H_5NH_2$	$\kappa_{50} \cdot 10^{-3}$	$\eta_{50} \cdot 10^{-3}$	$\kappa \cdot \eta \cdot 10^{-5}$
6.48	3.906	1.83	0.7148
10.30	4.916	2.65	1.303
17.29	6.349	4.10	2.603
21.41	6.717	4.95	3.325
25.72	6.654	5.40	3.593
32.02	5.934	5.53	3.282
30.75	5.874	5.55	3.261
33.63	6.261	5.49	3.437
39.00	5.807	4.95	2.874
41.97	5.206	4.66	2.426
47.90	3.667	4.04	1.481
53.33	2.442	3.59	0.876
63.18	0.873	3.00	0.262
73.15	0.114	2.60	0.0297
87.47	0.0048	2.19	0.00105

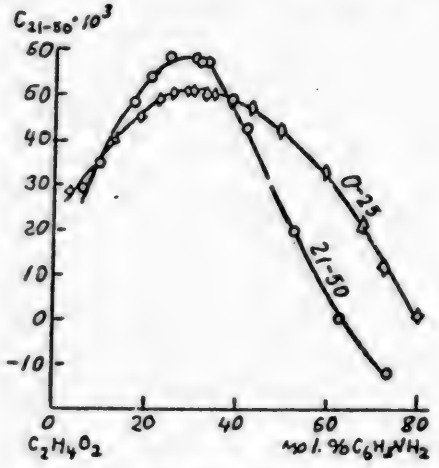

Fig. 2. Temperature coefficient of conductivity.

The drawing shows that the internal friction has a negligible effect upon the shape of the isotherms of specific conductivity at the given temperature, merely making the maximum more sharply defined. The "reduced" curves plotted by Klochko and Chanukadze show, moreover, that raising the temperature lowers the conductivity, and that the point of inflection present on the conductivity isotherms (uncorrected for viscosity) at low temperatures vanishes when the influence of that factor is eliminated.

A somewhat unusual behavior of this system attracts our attention: the maximum of the viscosity isotherm is shifted with rising temperature toward the less viscous component, i.e., $C_2H_4O_2$, as has been shown by the research of Klochko, for example, and contrary to the rule established by Kurnakov [20]. This departure from the usually observed rule is probably due to the fact that shift of the maximum is affected by the viscosity of the stably associated acid, which changes but little with temperature. We have established

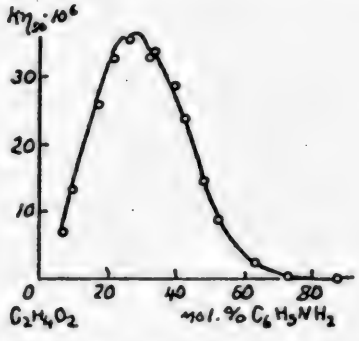

Fig. 3. Isotherm of corrected conductivity.

this relationship on the basis of Klochko's figures (Table 3).

We have plotted the curves of several properties in a single diagram (Fig. 4) in order to compare the results of our researches on the conductivity of the $C_2H_4O_2$ – $C_6H_5NH_2$ system with the data reported by other authors.

I – Fusibility curve (Pushin and Rikovsky) [18]; II – viscosity isotherm (Klochko); III – conductivity (ours); IV – departure of the refractive index from additivity (Pushin and Matavuly) [18]; V – temperature coefficient of conductivity (ours); VI – density; and VII – temperature coefficient of viscosity (Klochko and Chanukadze).

TABLE 3

Temperature	Change of viscosity with temperature as against η at 0°.	
	$C_2H_4O_2$	$C_6H_5NH_2$
15°	to 15%	to 47%
35	to 46.3	to 72
75	to 67.4	to 88

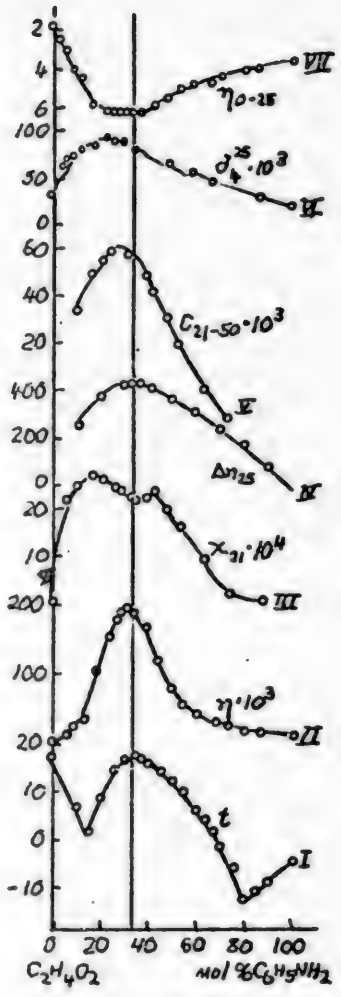

Fig. 4. Summary diagram of various properties of the system.

SUMMARY

1. The conductivity of the $C_2H_4O_2$ – $C_6H_5NH_2$ system has been investigated at 21 and 50°. The existence of a point of inflection in the conductivity isotherms, at about 33 mol % of aniline, is a reason for assuming the formation of the compound $C_6H_5NH_2 \cdot 2C_2H_4O_2$ within the system, the presence of this compound being an important factor in determining the system's conductivity.*

2. The curve of the temperature coefficient of conductivity also has a maximum at 33 mol % of aniline, thus confirming the existence of the compound $C_6H_5NH_2 \cdot 2C_2H_4O_2$ in the system.

3. The summary diagram of various properties of the system (Fig. 4) likewise testifies to the formation of a compound of the given composition, since the extreme values of the curves of the various properties either lie on or are close to the ordinate that corresponds to a 1:2 ratio of the components (1 mole of $C_6H_5NH_2$ and 2 moles of $C_2H_4O_2$.

* As we know, acetanilide is formed at high temperatures owing to the interaction of the components. But acetanilide cannot be taken as an electrolyte in this system, since even the research of Konavalov has shown that acetanilide has a negligible effect upon the conductivity.

4. The rather clear reflection of the chemical action in the diagrams of the investigated properties of the system indicates that the clearly marked alkaline nature of one component (aniline) and acid nature of the other ($C_2H_4O_2$) bring about considerable chemical interaction, forming a rather stable exothermic compound.

5. The existence of considerable chemical interaction in the system justifies the assumption that dimers of an acid decompose fairly readily when diluted with aniline, the simple molecules of the acid reacting with the molecule of aniline with no appreciable delay. (As has already been noted, the dimers of acetic acid do not enter into addition reactions.) It is evident, therefore, that the phenomenon of association has a negligible effect on the behavior of the system as a whole. It may be supposed that this effect is manifested, for instance, in the circumstance that the maximum of the viscosity isotherm shifts with rising temperature toward the less viscous acid, and not toward the more viscous aniline, as might have been expected [20].

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THE ELECTRICAL CONDUCTIVITY OF THE ACETIC ACID–PYRIDINE SYSTEM. II

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Fairly extensive experimental data are available on this system. Research has been done on its conductivity [1,2,3,4,5], its viscosity [6,7,8,9,10,11], its density [6,7,11], its vapor tension [12], its fusibility [13 14], its surface tension [15,16,17], its refractive index [12,18,19], its magnetic susceptibility [20], and its magnetic rotation of the plane of polarization [21]. In addition, the boiling point of the system has also been investigated [22,23].

Examination and comparison of the data obtained by various authors in their study of the conductivity of the $C_2H_4O_2$ – C_5H_5N system indicates that it is very hard to draw any definite conclusion from these data regarding the composition of the compounds formed in the system. The most complete investigation of the system's conductivity, at two different temperatures, was made by Puschin and Tutundzic [4], who concluded from their data that it was impossible to determine the composition of the compounds formed. In order to convince ourselves of the correctness of these conclusions, we used their data to compute the values of the relative temperature coefficient of conductivity, and then plotted the results of computation graphically. The plotted curve had a complicated and rather indeterminate form. It passed through two maxima, with a minimum between them. In the assumption that such an unusual course of the conductivity temperature coefficient was the result of some inaccurate and not entirely complete determinations, we resolved to investigate the conductivity in full ourselves in order to learn whether the diagram of the conductivity temperature coefficient actually looked like that. Moreover, we were interested in finding out the extent to which the presence of newly synthesized compounds, the existence of which was confirmed by almost all the previous authors, was reflected in this diagram.

As in our preceding research project, our goal was the tracing of the effect of the breakdown of the dimers of acetic acid upon the behavior of the given system by means of the composition – property diagrams and, in particular, by means of the conductivity and its temperature coefficient.

EXPERIMENTAL

The acetic acid was purified as in the preceding investigation. The pyridine was first desiccated for a long time with potassium hydroxide, after which it was distilled into ampoules that were then sealed. The pyridine (b.p. 115-116° at 763 mm) was kept in these ampoules until used in the experiment. Measurement of the electrical conductivity was done by the usual Kohlrausch method. It was measured as soon as the mixture had been prepared, although no noticeable change in the conductivity with the passage of time was observed. Mixing the $C_2H_4O_2$ and the C_5H_5N was accompanied by the evolution of heat.

The conductivity was measured at 28 and 50°. The results and the relative temperature coefficient calculated from them are listed in Table 1.

TABLE 1

Test No.	Mol. % $C_2H_4O_2$	$K_{28} \cdot 10^{-4}$	$K_{50} \cdot 10^{-4}$	$C_{28-50} \cdot 10^{-3}$
1	23.30	0.2516	0.3386	15.72
2	30.20	0.4869	0.6814	18.15
3	34.67	0.7678	1.0970	19.49
4	40.71	1.5880	2.2470	18.86
5	43.07	1.7490	2.4870	19.18
6	49.06	4.5490	6.0850	15.35
7	60.95	18.360	23.560	12.58
8	66.58	32.980	41.960	12.38
9	71.12	54.120	70.05	13.38
10	73.47	58.530	80.10	16.75
11	82.27	79.120	110.70	18.14
12	85.44	76.230	105.80	17.63
13	88.69	70.410	97.87	17.73
14	95.14	55.870	73.00	13.94

The variation of the specific conductivity with composition is illustrated in Fig. 1. The dotted line in the figure represents one of the isotherms (for 28°) plotted by Trifonov and Cherbov. The drawing shows that the conductivity isotherms are smooth, with a maximum at about 83 mol% of $C_2H_4O_2$. The position of the maximum does not shift (noticeably) as the temperature is changed. It likewise follows from the same drawing that the conductivity values obtained by Trifonov and Cherbov for mixtures containing up to 60 mol % of acid coincide with our values; their values for the conductivity of mixtures with higher percentages of acid are lower than ours. The reason for this discrepancy may be that these authors did not investigate the conductivity of the system for acetic-acid percentages above 60% with sufficient thoroughness. The maximum conductivity found by us and by Puschin is of the same order of magnitude.

Figure 2 illustrates the temperature coefficient of conductivity (C) as a function of the composition. The same figure reproduces curves of the conductivity temperature coefficient computed from the data of Trifonov and Cherbov (circles) and Puschin and Tutundzic (dots). Figure 2 shows that the curve of the conductivity temperature coefficient actually has a complicated shape, passing

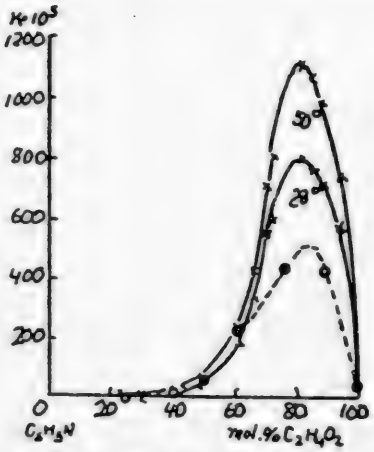

Fig. 1. Conductivity as a function of composition.

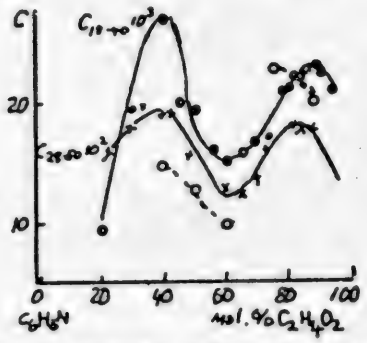

Fig. 2. Temperature coefficient of conductivity

through two maxima and one minimum. One maximum is located at nearly 40 mol % of acid, as in the Puschin curve, whereas the other has a somewhat different location than on the curve of the authors cited, lying at approximately 83 mol % of acid; the minimum is near the 60 mol % of acid. Thus the existence of two maxima on the conductivity temperature coefficient curve leads us to assume that two compounds of the following composition:

1. $3\ C_5H_5N \cdot 2C_2H_4O_2$,
2. $C_5H_5N \cdot 4C_2H_4O_2$,

are formed in the liquid phase of the given system. The ordinate of the second of the foregoing compounds corresponds to that of the maximum on the conductivity isotherm.

To judge by Faust's data [7], the viscosity curve has one of its branches (in the $C_2H_4O_2$ region) concave upward, away from the composition axis, whereas both branches are usually concave downward.

Viscosity has practically no effect upon the shape of the conductivity isotherm.

The curve of this property, like that of the conductivity isotherm, passes, through a maximum at about 83 mol. % of acid, and for that reason reducing the conductivity to constant viscosity (Table 2) is not reflected in the conductivity curve and does not cause any shift in the latter's maximum (Fig. 3).

TABLE 2

Mol. % $C_2H_4O_2$	Specific conductivity, $K_{28} \cdot 10^{-3}$	Viscosity, $\eta_{28} \cdot 10^{-3}$	$K_{28} \cdot \eta_{28} \cdot 10^{-5}$
30.20	0.04869	15.13	0.0735
34.67	0.07678	16.25	0.1247
40.71	0.1588	15.94	0.2531
48.26	0.3942	23.45	0.9242
60.95	1.836	28.99	5.323
63.18	2.150	37.00	7.954
73.12	5.853	40.35	23.621
74.47	6.851	35.40	24.253
82.27	7.912	44.75	35.410
85.44	7.623	43.66	33.280
88.69	7.041	37.52	26.420
95.14	5.587	22.16	12.380

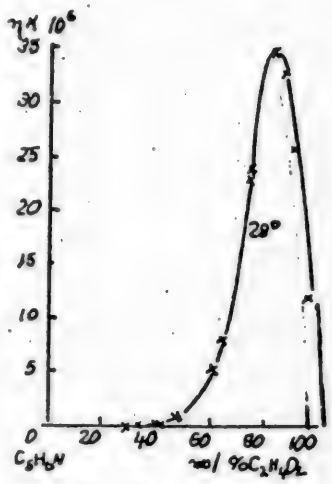

Fig. 3. Conductivity isotherm, corrected for viscosity.

Thus, in the given system the ordinate corresponding to the compound $C_5H_5N \cdot 4C_2H_4O_2$ represents the maximum value of both viscosity and conductivity, notwithstanding the fact that viscosity and conductivity are, as we know inversely proportional to each other. This may be explained, apparently, as follows: the compound formed possesses some singlular properties. It has considerable conductivity, together with high viscosity and the resultant low mobility of its ions.

Swearingen also mentions the existence of the compound $C_5H_5N \cdot C_2H_4O_2$ in the system [5,14,11,22].

In addition to its maxima, the curve of the temperature coefficient of

conductivity possesses a minimum, which likewise corresponds to one of the stoichiometric ratios of the system components. This minimum corresponds to the compound $2C_5H_5N \cdot 3C_2H_4O_2$, the existence of which is corroborated by the research of other authors as well [6,24,22,23].

Thus, the measurements of the conductivity of the $C_2H_4O_2 \cdot C_5H_5N$ system justify the hypothesis that three compounds of the following composition:

1. $3C_5H_5N \cdot 2C_2H_4O_2$,
2. $2C_5H_5N \cdot 3C_2H_4O_2$,
3. $C_5H_5N \cdot 4C_2H_4O_2$,

are formed by the reaction of the components with each other.

We have combined the curves of all the properties of this system in a single diagram (Fig. 4) to facilitate comparison of our results with those obtained by other authors.

Fig. 4 shows that the ordinate for the compound $C_5H_5N \cdot 4C_2H_4O_2$ corresponds or is close to the maximum of the curves for all the properties cited, with the exception of the vapor-tension and fusibility curves. These two latter diagrams indicate the existence of a compound within the system, $C_5H_5N \cdot C_2H_4O_2$, which is in no way shown on the curve of the temperature coefficient of conductivity. Neither the first nor the second of the foregoing compounds makes itself felt in the cited curves.

In their study of the departure of the refractive index from additivity, Puschin and Matavuly mention the existence of the compound $C_5H_5N \cdot 3C_2H_4O_2$ within the system. But the shape of the curve showing the variation of the maximum departure from additivity with composition demonstrates that the maximum lies at 80 mol % of acid, i.e., at an ordinate corresponding to a compound $C_5H_5N \cdot 4C_2H_4O_2$.

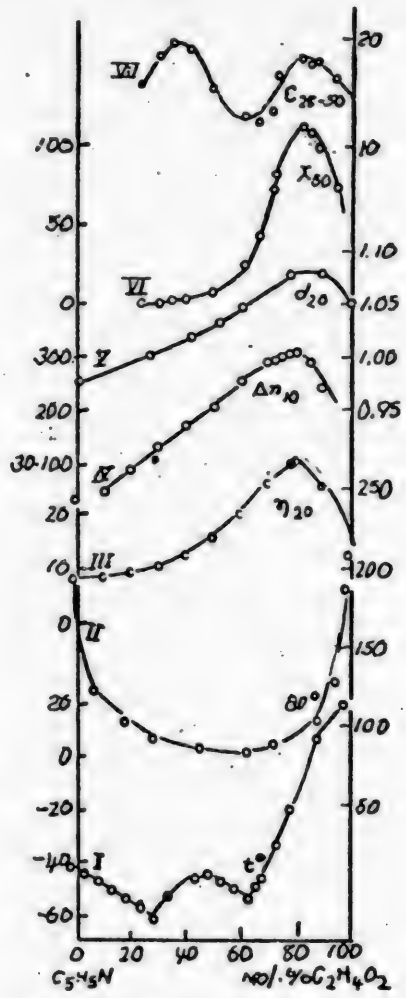

Fig. 4. Summary diagram of various properties of the system.

I-Fusibility diagram (Puschin and Rikowski); II- Vapor-tension curve (Zawidski); III-Viscosity isotherm (Faust); IV-Curve showing the departure of the refractive index from additivity (Puschin and Matavuly); V-Density isotherm (Tsakalotos); VI-Curve of specific conductivity; VII-Temperature - coefficient curve (Naumova).

SUMMARY

1. The electrical conductivity of the $C_2H_4O_2$-C_5H_5N system has been investigated at 28 and 50°. The curves of specific conductivity are smooth, with a maximum at about 83 mol % of acid.

2. The diagram of the temperature coefficient of conductivity has an unusually complicated shape. The extremes (two maxima and one minimum) correspond to three different stoichiometric ratios of the components.

3. Though the presence of chemical action is shown clearly enough in the composition-property diagrams, deciphering the composition of the compound formed is rather difficult. This is probably due to the fact that in this system several compounds are formed, some of which are rather unstable.

4. The aggregate of the results of research on the conductivity and other properties of the $C_2H_4O_2$–C_5H_5N system indicates the possible formation of the following four compounds within it:

1. $3C_5H_5N \cdot 2C_2H_4O_2$,
2. $2C_5H_5N \cdot 3C_2H_4O_2$,
3. $C_5H_5N \cdot 4C_2H_4O_2$,
4. $C_5H_5N \cdot C_2H_4O_2$.

5. There is no doubt of the existence of two compounds ($C_5H_5N \cdot 4C_2H_4O_2$ and $2C_5H_5N \cdot 3C_2H_4O_2$), since the ordinate of the first one (Fig. 4) corresponds to the maximum of most of the properties investigated, which cannot be an accident.

The existence of the second compound has been proved by Swearingen [22], Graner [23], and Andre [24], even though this compound does not make itself felt in the fusibility diagram.

6. The existence of the compounds $3C_5H_5N \cdot 2C_2H_4C_2$ and $C_5H_5N \cdot C_2H_4O_2$ cannot be asserted with certainty; the presence of the former is not exhibited in any diagram, with the sole exception of the curve for the temperature coefficient of conductivity. The latter compound ($C_5H_5N \cdot C_2H_4O_2$) was discovered by thermal analysis. We did not have Swearingen's fusibility diagram [14] at hand, and the points on Puschin's and Rikowski's curve [13] are spaced rather far apart, as is the case in Zawidzki's vapor-tension curve [12]. Hence, we have no confidence that the curves have this very shape, or that their "singular" points correspond to the ordinate of the compound $C_5H_5N \cdot C_2H_4O_2$, especially since the melting points found by Swearingen and Puschin are very far apart (-59° and -46°).

7. The experimental data justify the conjecture that the process of breaking down the dimers of acetic acid has no appreciable effect upon the behavior of the system, since this decomposition takes place fairly intensively when pyridine is mixed with the acid (provided the latter is not present in excess) and offers no obstacle to chemical reaction between the components (the dimers of acetic acid do not enter into addition reactions). When there is not enough pyridine present, it must be assumed that the acid exists largely in the form of dimers, since the portion of the viscosity curve that is situated in the acid region is convex upward, which is somewhat unusual [7]. The shift of the maximum on the viscosity curves with rising temperature is likewise out of the ordinary, taking place in the direction of the less viscous $C_2H_4O_2$. This is probably due to the fact that the shift of the maximum is affected by the acetic acid, and not by the pyridine, since the viscosity of the stably associated acid changes but little as the temperature is raised [7].

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ELECTRICAL CONDUCTIVITY AND VISCOSITY OF THE ACETIC ACID-NITRIC ACID SYSTEM. III

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It is known that in aqueous solution nitric acid is somewhat stronger than acetic acid.

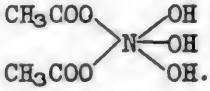
The literature contains references to the fact that when these acids are mixed together, they interact chemically, forming certain chemical compounds [1,2,3]. Pictet and Genequand [1], for instance, point out in their researches that if the mixture consists of two molecules of acetic acid to each molecule of nitric acid, the whole mass distills over at the constant temperature of 127-128°.

Analysis of the product thus formed indicated that its composition may be expressed by the following formula:

$$C_4H_9NO_7 \ (HNO_3 \cdot 2C_2H_4O_2).$$

The authors obtained the same product by mixing acetic anhydride with nitric acid, sp. gr. 1.4.. Pictet and Genequand also determined the molecular weight of mixtures of HNO_3 and $C_2H_4O_2$ cryoscopically.

Their research led them to conclude that this product is an exothermic compound with the structural formula:



This compound was called diacetyl nitric acid. It is a liquid that fumes in air, with a boiling point of 127.7° (at 730 mm), a sp. gr. of 1.197 at 15°, and 1.189 at 23°, and a refractive index of n_D 1.38432, at 23°. It mixes with water in any proportions, with the evolution of a slight amount of heat, and usually reacts violently with organic compounds.

Hantzsch [2], who observed the absorption of ultraviolet light by acids, their esters, and their salts, also mentions the existence of a compound of this composition in the system. Hantzsch assigns it the following formula:

$$(CH_3COOH)_2HONO_2.$$

Briner and his associates [3], in their determinations of the density, vis- and fusibility of mixtures of anhydrous acetic and nitric acids, presuppose the formation of the equimolecular compound ($HNO_3 \cdot C_2H_4O_2$). They also investigated the Raman spectra of this system. Since lines were found in the spectogram that corresponded to the constituents of the mixture, the authors concluded that the substance formed was an addition product in which each acid retains its characteristic properties.

Kolthoff and Wileman [4] investigated the conductivity of this system, though not over the entire range of concentrations, confining themselves to the region of high percentages of $C_2H_4O_2$ at a single temperature. The only thing that is clear from the experimental data obtained by these authors is that the specific conductivity of the system increases as the quantity of HNO_3 is increased.

Thus the literature contains references to the possibility of the formation of two compounds of the following composition:

1) $HNO_3 \cdot 2C_2H_4O_2$,

2) $HNO_3 \cdot C_2H_4O_2$,

within the system.

We were interested in finding out whether the presence of these compounds in the system is reflected in the conductivity diagram, as well as the extent to which this diagram indicates the chemical action occurring in the system, the components of which are associated and possess acid properties in aqueous solution that are only slightly different.

Besides the conductivity, we also determined the viscosity of the system.

Electrical Conductivity of the $HNO_3 - C_2H_4O_2$ System

Absolute acetic acid was prepared, as in our previous researches, by repeated fractional freezing in ampoules

The nitric acid was purified by the method developed by K.P Mishchenko [5], i.e., by distillation in vacuum from a mixture with sulfuric acid. The absolutely colorless acid obtained was at once sealed into ampoules, in which it was stored. At 25°, the nitric acid had a specific conductivity of $3.4 \cdot 10^{-3}$ mho. The conductivity was measured in a few containers with an electrolysis volume of 0.7183 to 2.582. Heat was evolved when the acids were mixed together.

The conductivity of the $HNO_3 - C_2H_4O_2$ system was measured at 0 and 25°. The results of our measurements are listed in Table 1, the change in the specific conductivity with solution concentration, expressed in molecular percentages of $C_2H_4O_2$, being depicted in Fig. 1.

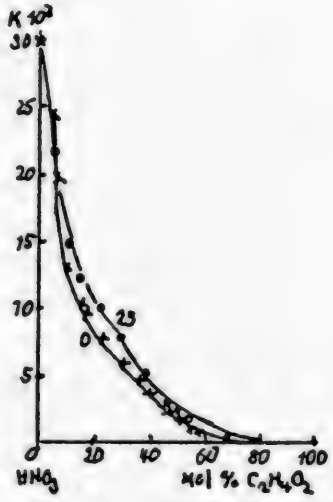


Fig. 1. Conductivity as a function of composition.

It is seen in the figure that the conductivity drops from 10^{-2} mho to 10^{-5} mho as the percentage of acetic acid in the mixture is increased, this drop being more rapid at 0° than at 25°. Both of these isotherms are curves that are concave upward throughout their length. Neither curve has any singular points (maximum, minimum, point of inflection). Tartakovskaya [6] obtained similar curves when she studied the conductivity of systems in which no chemical action takes place between the components, one of the components being associated and possessing a conductivity of its own. Hence, to judge by the conductivity diagram, we gain the impression that there is no chemical action in the $C_2H_4O_2 - HNO_3$ system either. Further investigation proved the contrary to be true, however.

Thus, the temperature coefficient of conductivity (C) was calculated for the 0-25° range. Its values are likewise listed in Table 1. The variation of the temperature coefficient of conductivity with composition is plotted in Fig. 2.

The drawing shows that the temperature coefficient of conductivity drops fairly slowly in the region of high concentrations of acetic acid, down to about 67 mol % of $C_2H_4O_2$. As dilution progresses still further, this drop becomes

TABLE 1

Test No.	Molecular % of $C_2H_4O_2$	$\chi_0 \cdot 10^{-4}$	$\chi_{25} \cdot 10^{-4}$	$C_{0-25} \cdot 10^{-3}$
1	0	327.9	347.24	2.359
2	4.00	241.2	—	—
3	5.78	197.1	217.40	4.120
4	10.11	132.3	147.9	4.717
5	15.76	103.6	122.0	7.104
6	17.69	97.62	—	—
7	21.97	77.91	101.2	9.883
8	30.65	58.32	78.99	14.180
9	36.71	49.14	68.49	15.750
10	39.84	35.81	52.22	18.330
11	46.60	22.00	32.49	19.070
12	51.06	16.42	25.25	21.51
13	55.13	9.946	16.26	25.39
14	57.24	9.870	16.21	25.69
15	68.62	2.381	4.097	28.53
16	81.29	0.409	0.7186	30.26
17	83.52	0.261	0.4616	30.80
18	90.87	0.0523	0.1056	31.26

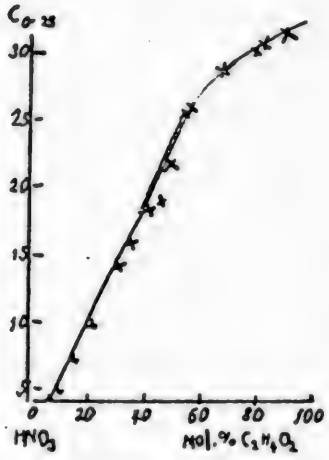


Fig. 2. Temperature coefficient of conductivity.

steeper, turning into a straight line. Hence, there is a point of inflection on the curve at 67 mol. % of $C_2H_4O_2$, since the course of the curve changes sharply at this point.

Thus, the curve of the temperature coefficient of conductivity confirms our assumption that mixing the system's components together causes chemical interaction; moreover, as the curve of the conductivity temperature coefficient indicates, this interaction results in the formation of the compound $HNO_3 \cdot 2C_2H_4O_2$, the existence of which was asserted by Hantzsch [2] and Pictet [1]. We were unable to detect the second of the presumptive compounds, $HNO_3 \cdot C_2H_4O_2$ (Briner) [3], in the curve of the temperature coefficient of conductivity

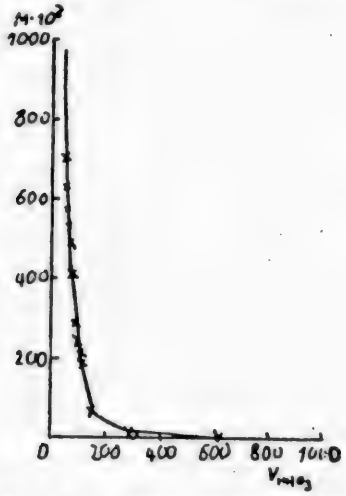


Fig. 3. Molecular conductivity, based on HNO_3 as the electrolyte.

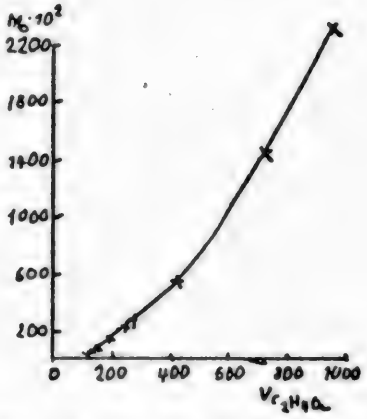


Fig. 4. Molecular conductivity, based on $C_2H_4O_2$ as the electrolyte.

To obtain further proof of the presence of chemical interaction between the system's components, we computed the molecular conductivity (μ), taking first one and then the other acid as the electrolyte.

The calculation results are given in Table 2 and plotted graphically in Figs. 3 and 4.

TABLE 2

Per cent by wt. of $C_2H_4O_2$	$C_2H_4O_2$ (ν)	$C_2H_4O_2$ (μ)	HNO_2 (ν)	HNO_2 (μ)
4.20	946.5	22.830	–	–
5.55	723.9	14.270	45.07	0.9798
9.67	419.1	5.544	47.77	0.7065
15.12	272.3	2.821	52.01	0.6346
17.00	244.3	2.362	–	–
21.15	199.1	1.551	56.87	0.5755
29.62	146.2	0.8528	65.82	0.5199
34.25	129.2	0.6348	72.04	0.4934
38.68	115.8	0.4146	78.13	0.4080
45.39	100.8	0.2218	89.91	0.2921
49.85	93.45	0.1535	99.94	0.2523
53.91	87.54	0.08716	110.10	0.2093
56.04	84.97	0.08386	116.30	0.1886
66.00	75.19	0.01790	157.00	0.0644
80.54	65.06	0.00266	289.00	0.0208
82.84	63.48	0.001652	328.00	0.01514
90.43	60.32	0.00358	626.60	0.00662

Our experimental results indicate that both of the curves of molecular conductivity are concave upward and, hence, do not at all conform to Ostwald's dilution law. The curve of molecular conductivity (Fig. 3) based upon nitric acid as the electrolyte is a typically anomalous curve, dropping steeply within a narrow dilution interval. With further dilution, (beyond 100 liters), its drop slows down. Thus, nitric acid, which is a rather strong electrolyte in aqueous solutions, behaves like a nonelectrolyte in this system [7,8]. The same is true of acetic acid, as is testified to by the anomalous nature of the curve of molecular conductivity (Fig. 4) based on acetic acid as the electrolyte. Compared to nitric acid, acetic acid behaves in aqueous solutions like a weaker electrolyte; but in our system this anomaly is less markedly evident.

Hence, the data on the conductivity of the $HNO_3 - C_2H_4O_2$ system corroborates the presence of chemical interaction between the components and the formation of only one compound, $HNO_3 \cdot 2C_2H_4O_2$, which is an electrolyte.

Viscosity of the $C_2H_4O_2 - HNO_3$ System

We investigated the viscosity at the same temperatures as the conductivity.

Measurement was done with an Ostwald viscosimeter, whose open ends were connected together by rubber tubing via a three-way stopcock. This protected the system against evaporation and the influence of the surrounding environment.

We likewise measured the density of the system. The data on viscosity and density are listed in Table 3. The viscosity values are plotted graphically in Fig. 5.

The diagram indicates that the viscosity of the system changes considerably with changes in temperature. The viscosity isotherms are somewhat unusual, for both branches of the curve are concave downward, whereas isotherms usually are concave upward. The curves have a maximum that shifts as the temperature drops toward the compound:

$$HNO_3 \cdot 2C_2H_4O_2 \text{ (67 mol. \% } C_2H_4O_2).$$

The maximum of the 0° isotherm is somewhat sharper. Thus, the viscosity diagram also testifies to the existence of the foregoing compound in the solution.

This change in viscosity must doubtless affect the behavior of the specific conductivity as the system composition is changed. To convince ourselves of the

TABLE 3

Molecular % of $C_2H_4O_2$	Density		Viscosity	
	0°	25°	0°	25°
0.00	–	–	0.01100	–
4.00	1.510	1.485	0.01280	0.008776
15.76	1.457	1.427	0.01752	0.010860
17.69	1.445	1.420	–	–
21.99	–	–	0.02090	–
30.65	1.376	1.352	0.02774	0.01480
39.84	1.340	1.315	0.03069	0.01670
46.60	1.311	1.283	0.03247	0.01728
51.06	1.288	1.257	0.03401	0.01768
55.64	1.260	1.234	–	0.01874
58.82	1.246	1.224	0.03559	0.01856
65.69	1.217	1.192	–	–
68.62	1.209	1.180	0.03499	0.01825
70.67	1.198	1.174	0.03461	0.01801
81.29	1.145	–	0.03214	–
83.52	1.141	1.119	0.02922	0.01644
90.87	1.100	1.075	–	0.01411

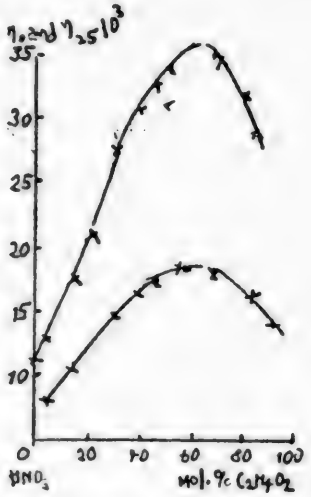


Fig. 5. Viscosity isotherms.

TABLE 4

Molecular per cent of $C_2H_4O_2$	$\kappa \cdot \eta \cdot 10^{-4}$	
	0°	25°
5.78	2.621	1.883
10.11	1.998	1.464
15.76	1.815	1.325
21.98	1.822	1.275
30.65	1.618	1.169
39.84	1.099	0.872
46.60	0.714	0.561
51.06	0.5587	0.4454
68.62	0.0883	0.0 48
81.29	0,0132	–
83.52	0.0076	0.00759
90.87	0.00143	0.00149
0	3.3000	–

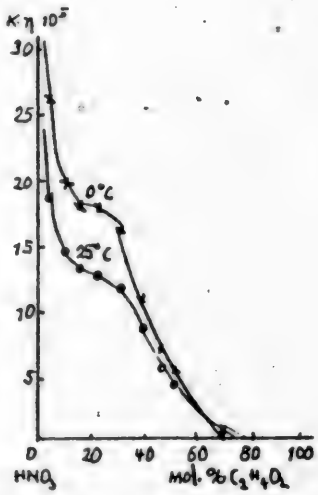


Fig. 6. Isotherms of corrected conductivity.

correctness of this hypothesis, we eliminated this effect. This correction yielded the values that are given in Table 4 and shown graphically in Fig. 6.

The figure indicates that the curves of the so-called "reduced" conductivity at both temperatures are different from the uncorrected curves. Such a shape of the conductivity isotherms may be explained as follows: interaction between the system's components results in the formation of an electrolyte with a conductivity that is higher than that of one of the components ($C_2H_4O_2$). Thus, the conductivity of the system must be made up of the conductivity of the acids and of a newly formed compound, with the conductivity of the HNO_3 doubtless predominating in the region of its high concentrations, and the conductivity of the coordination compound affecting the course of the isotherm most at the component ratios at which most of this

compound is formed. As the diagram indicates, this occurs at a concentration of 22 mol. % of $C_2H_4O_2$. It might be thought that the presence of the coordination compound will be most clearly manifested if we annul the considerable effect of the conductivity of HNO_3 upon the conductivity of the system. To check this, we made use of Tartakovskaya's experimental data. She investigated the electrical conductivity of the HNO_3 – $CH_2ClCOOH$ system. Her data, and the data of others, led her to conclude that there is no chemical action present in the system, its conductivity being governed actually by the conductivity of the nitric acid, which diminishes when diluted with the second component as a result of the decomposition of the complex electrolyte $(HNO_3)_x$ into simple nonionogenic molecules of HNO_3.

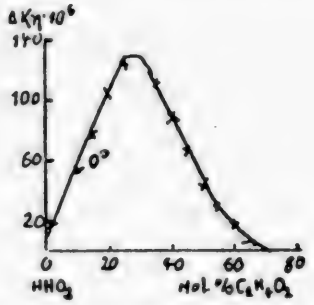


Fig. 7. Difference between the corrected conductivities.

TABLE 5

Molecular percent $C_2H_4O_2$	$\chi_0\eta_0\cdot10^{-4}$		$\Delta\cdot\chi_0\cdot\eta_0\cdot10^{-4}$
	Tartakovskaya's data	Our data	
1	3.04	3.20	0.16
5	2.12	2.60	0.48
10	1.42	1.96	0.54
15	1.05	1.83	0.78
20	0.75	1.80	1.05
25	0.49	1.74	1.25
30	0.30	1.59	1.29
35	0.19	1.31	1.12
40	0.14	1.03	0.89
45	0.10	0.77	0.67
50	0.08	0.55	0.47
55	0.06	0.36	0.30
60	0.04	0.23	0.19
70	0.02	0.07	0.06

Subtracting Tartakovskaya's figures for the "reduced" conductivity of the HNO_3 – $CH_2ClCOOH$ system from the corresponding figures of ours for the HNO_3 – $C_2H_4O_2$ system, we obtained the difference $(\Delta\eta\cdot\kappa)$, the values of which are given in Table 5 and shown graphically in Fig. 7.

The figure shows that the curve has a sharply marked maximum (at about 33 mol.% $C_2H_4O_2$), thus confirming the presence of chemical action in the system and the formation of an electrolyte.

SUMMARY

1. The electrical conductivity and the viscosity of the HNO_3 – $C_2H_4O_2$ system has been investigated at the temperatures of 0 and 25°.

2. The maximum on the viscosity isotherms and the point of inflection in the curve of the temperature coefficient of conductivity indicate the existence of an exothermic compound with the composition $HNO_3\cdot2C_2H_4O_2$ within the system. Its presence is not reflected in the isotherms of specific conductivity because this compound is a weak electrolyte, owing to the complex structure of its molecule.

3. The presence of chemical interaction in the system is detected in the conductivity isotherms only when the effect of viscosity upon this property is eliminated. The singular points on the diagrams of "reduced" conductivity and of the difference between the two "reduced" conductivities are situated in the region of high HNO_3 percentages, i.e., they do not correspond to any of the conjectured compounds.

4. It is possible that the discrepancy between the locations of the singular

points in the foregoing diagrams (Figs. 6 and 7) and the ordinate of the hypothetical compounds may vanish if allowance is made for the effect upon the behavior of the system of the decomposition of the associated $(C_2H_4O_2)_2$ molecules. With dilute nitric acid, this decomposition may be not intensive enough owing to the slight difference between the strengths of the acids making up the system, and hence the slight affinity between them. The dimers $(C_2H_4O_2)_2$ will be present in one quantity or another at all component ratios. A confirmation of this, for instance, is afforded by the viscosity isotherms (concave downward toward the composition axis instead of the usual [8] concave upward curves).

Thus, an appreciable decomposition of the $(C_2H_4O_2)_2$ molecules will be observed only in dilute solutions, in which the decomposing molecules yield a sufficient amount of the products of interaction with HNO_3; in our opinion, this is also reflected in the curves of the "corrected" conductivity (point of inflection) and of the difference between the two "corrected" conductivities (a maximum). This makes it obvious that if we make allowance for dimer molecules as well as simple ones when computing the molecular percentage of $C_2H_4O_2$, the singular points in the diagrams (Fig. 6 and 7) will agree more or less accurately with the composition of the compound $C_2H_4O_2 \cdot HNO_3$, the existence of which is likewise supported by Briner and Favarger [3].

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COORDINATION COMPOUNDS OF BIVALENT METALS WITH DIMETHYLAMINOANTIPYRINE (PYRAMIDON)

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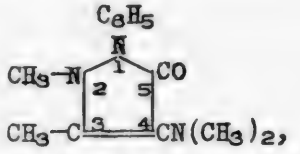
Dimethylaminoantipyrine, dimethylaminodiphenylpyrazolone, or pyramidon, with the formula:



was first synthesized in 1893 by Stolz. It is a white crystalline powder with a melting point of 108°, which dissolves in 18 parts of cold water and is readily soluble in alcohol or benzene. In 1945 a paper by D.I.Ryabchikov and E.A.Terentyeva [1] described the synthesis of coordination compounds of pyramidon and antipyrine with trivalent rare-earth metals, with the general formula: $[Me(C_{13}H_{17}ON_3)_3]X_3$ and $[Me(C_{11}H_{12}ON_2)_6]X_3$, where Me = La, Ce, Pr, etc., and X = Cl', NO_3', and ClO_4'. In the same paper it was shown that the pyramidon molecule occupies two coordination positions and, hence, effects its bond with the central metal atom via the nitrogen atoms and the methyl groups attached to them.

The literature available to us did not enable us to establish the existence of coordination compounds of pyramidon with bivalent metals.

We have proved experimentally that in most instances pyramidon coordination compounds can be prepared by the reaction of the corresponding metals with aqueous solutions of pyramidon. It was found that the medium in which the reaction was carried out was of material importance – whether it was acid or neutral. In a neutral medium, the formation of the inner sphere, part of which is constituted by the pyramidon molecules coordinated about the central metal atom, takes place more or less vigorously, with one or two molecules of pyramidon coordinated.

The reactions between a salt of a bivalent metal and pyramidon may take place in accordance with the following equations:

$$MeX_2 + Pyr = [Me(Pyr)]X_2$$

or

$$MeX_2 + 2Pyr = [Me(Pyr)_2]X_2,$$

where: Me = Zn^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{+2}, Ni^{2+}, and Hg^{2+}, Pyr = $C_{13}H_{17}ON_3$; and X = CNS', Cl', Br', and I'.

Moreover, several coordination compounds may be synthesized by the exchange of one anion for another in the outer sphere in accordance with the following equation:

$$[Me(Pyr)_2]X_2 + 2R' = [Me(Pyr)_2]R_2 + 2X',$$

where: X = Cl', CH_3COO', or NO_3'; and R = CNS', Br', or I'.

It has also been demonstrated in our laboratory [2] that in an acid solution the reaction of synthesizing the complex salt may be expressed by the following

schematic equation:

$$2Pyr + 2H^+ + Me^{+2} + 4X' = [Pyr]_2[Me(X)_4],$$

where: Me = Zn^{2+}, Cd^{2+}, Mn^{2+}, Pd^{2+}, and X' = CNS', I', and Br'.

Most of the coordination compounds, synthesized in a neutral or acid medium, are only slightly soluble in water.

EXPERIMENTAL

In synthesizing the coordination compounds, we usually prepared an aqueous solution of pyramidon that was saturated at room temperature, i.e, approximately 5 g in 100 ml of water, which is about a 0.2 molar solution.

Synthesis of Dipyramidon Thiocyanates

Synthesis of dipyramidoncadmium thiocyanate. As a preliminary, we prepared 0.2 N solutions of cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$, or cadmium acetate $Cd(CH_3COO)_2 \cdot 3H_2O$, and of ammonium thiocyanate. Equal volumes of the two substances were poured together and heated to boiling, and a slight excess (over the theoretically computed quantity) of a hot solution of pyramidon was added to the mixture; a white crystalline precipitate was thrown down at once.

The product was recrystallized from hot water several times and then carefully dried at a temperature of about 100°.

The CNS group was quantitatively determined in the synthesized preparation.

Taken: 0.1546 g substance: obtained; 0.0752 g AgCNS.
Taken: 0.1496 g substance; obtained: 0.0722 g AgCNS.
Found %: CNS 17.02, 16.89.

The CNS calculated from the formula $[Cd(Pyr)_2](CNS)_2$ (mol. wt. = 691.143) is 16.81%.

Dipyramidonzinc thiocyanate was prepared in almost exactly the same manner; i.e., equal volumes of 0.2 N solutions of zinc acetate and ammonium thiocyanate were mixed together, and then an excess of pyramidon solution was added, the reaction taking place in the cold. The white precipitate was recrystallized several times from a hot aqueous solution and then dried.

The quantitative determination of the CNS yielded the following results:

Taken: 0.1362 g substance: obtained: 0.7020 g AgCNS.
Taken: 0.2190 g substance: obtained: 0.1122 g AgCNS.
Found %: CNS 18.035, 17.93.

The CNS calculated from the formula $[Zn(Pyr)_2](CNS)_2$ (mol. wt. = 644.11) is 18.03%.

We likewise synthesized dipyramidon ferrothiocyanate from freshly prepared ferrous sulfate, $FeSO_4 \cdot 7H_2O$. The reaction took place in the cold. We were unable to recrystallize the synthesized preparation owing to the rapid oxidation of the Fe^{2+} to Fe^{3+}, the substance taking on a red hue; we therefore confined ourselves to repeated decantation and rapid washing with water. Drying was done at a temperature of 75°.

Determination of the CNS group yielded the following results:

Taken: 0.1868 g substance: obtained: 0.0974 g AgCNS.
Taken: 0.1254 g substance: obtained; 0.0660 g AgCNS.
Found %: CNS 18.255, 18.40.

The CNS calculated from the formula, $[Fe(Pyr)_2](CNS)_2$, (mol. wt. = 634.58) is 18.30%.

It should be noted that one can also use Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, as an initial substance for synthesizing dipyramidon ferrothiocyanate.

The synthesized preparation is unstable, its crystals taking on a red hue after some time in contact with the air.

Besides the substances already listed, we also synthesized dipyramidon thiocyanates of Mn^{2+}, Ni^{2+}, and Co^{2+}.

The quantitative determination of the CNS in these substances yielded the following results.

Analysis of dipyramidonmanganese thiocyanate:

Taken: 0.2360 g substance: obtained: 0.1244 g AgCNS.
Taken: 0.1900 g substance; obtained: 0.1014 g AgCNS.
Found %: CNS 18.44, 18.67.

The CNS calculated from the formula, $[Mn(Pyr)_2](CNS)_2$, (mol. wt. = 633.66) is 18.33%.

Analysis of dipyramidon cobaltothiocyanate.

Taken: 0.1316 g substance; obtained: 0.0710 g AgCNS.
Taken: 0.1716 g substance; obtained: 0.0906 g AgCNS.
Found %: CNS 18.87, 18.47.

The CNS calculated from the formula $[Co(Pyr)_2](CNS)_2$, (mol. wt. = 637.67) is 18.22%.

Analysis of dipyramidon nickelothiocyanate.

Taken: 0.1716 g substance; obtained: 0.0900 g AgCNS.
Taken: 0.1280 g substance: obtained: 0.0680 g AgCNS.
Found %: CNS 18.35, 18.59.

The CNS calculated from the formula, $[Ni(Pyr)_2](CNS)_2$, (mol. wt. = 637.43) is 18.22%.

The properties of these coordination compounds are listed in Tables 1 and 2.

In addition to compounds of pyramidon thiocyanate, we also synthesized pyramidon chlorides, bromides, and iodides of bivalent metals.

Synthesis of Pyramidon Chlorides

Synthesis of pyramidonzinc chloride. Up to 8 g of zinc chloride was gradually added to 50 ml of a boiling, saturated solution of pyramidon. The solution was diluted with water, heated, filtered free of the cloudiness that formed, and carefully evaporated to small volume. The next day the precipitate was filtered out, washed several times with water, and dried at 80°.

Quantitative determination of the Cl yielded the following results:

Taken: 0.2096 g substance; obtained: 0.1642 g AgCl.
Taken: 0.2080 g substance; obtained: 0.1612 g AgCl.
Found %: Cl 19.38; 19.17.

For $[Zn(Pyr)]Cl_2$ (mol. wt. = 367.6), the calculated Cl = 19.29%.

Synthesis of dipyramidoncadmium chloride. Some 250 ml of a hot solution of pyramidon, saturated in the cold, was added to 20 ml of a solution of cadmium

TABLE 1

Property	$[Zn(Pyr)_2](CNS)_2$	$[Cd(Pyr)_2](CNS)_2$	$[Fe(Pyr)_2](CNS)_2$
Crystal color.....	White	White	Pale orange
Behavior in air.....	Stable	Stable	Oxidizes, crystals turning red
Solubility in H_2O, 15°	0.19 g in 100 ml	0.12 g in 100 ml	0.43 g in 100 ml
Solubility in C_2H_5OH..	0.13 g in 100 ml	0.074 g in 100 ml	0.346 g in 100 ml
Solubility in $(C_2H_5)_2O$	0.1 g in 100 ml	0.027 g in 100 ml	0.02 g in 100 ml
Behavior of saturated solutions of the substances with dilute H_2SO_4 and HNO_3.....	No changes	No changes	H_2SO_4 produces no effect; HNO_3 reddens the solution.
Behavior with NaOH....	Precipitate of $Zn(OH)_2$ dissolves in an excess of the precipitating agent	Slight white precipitate of $Cd(OH)_2$	Precipitate of $Fe(OH)_2$
Behavior of saturated solutions of the substances with $AgNO_3$ in the cold.....	A slight suspension of AgCNS is formed, and the solution turns pale yellow; when HNO_3 is added, a white, cottony precipitate appears.		Precipitate of AgCNS formed, after a time, solution turns blue, then black precipitate of silver appears — action of pyramidon.
Behavior with solutions of $FeCl_3$.....	Violet color appears — pyramidon is present. An excess of $FeCl_3$ produces a cherry red color — the thiocyanogen ion is present.		
Behavior of the dry substance when heated in a capillary	Fuses at 130°	Turns red at 198°, fuses at 214° with partial decomposition.	Turns dark at 185°, fuses at 202° to a brown liquid.
Electrical conductivity at 15°.....	$\mu_{1000} = 214$; $\mu_{2000} = 230$.	$\mu_{1000} = 208$; $\mu_{2000} = 240$.	$\mu_{1000} = 210$; $\mu_{2000} = 221$;
Appearance of the crystals under the microsope.....	Fig. 1	Fig. 2.	Fig. 3

chloride saturated while hot and containing about 11 g of $CdCl_2$. Forty-eight hours later the precipitate was filtered out, recrystallized from hot aqueous solutions, and dried.

Quantitative determination of the Cl yielded the following results:

Taken: 0.2344 g substance; Obtained: 0.1052 g AgCl.
Taken: 0.2286 g substance; Obtained: 0.1022 g AgCl.
Found %: Cl 11.10, 11.06.

For $[Cd(Pyr)_2]Cl_2$ (mol. wt. = 645.93), the calculated Cl was 10.98%.

Synthesis of pyramidonmercury dichloride. 80 ml of a solution of pyramidon, saturated in the cold, was added to the same quantity of a 0.2 N solution of mercuric chloride. The precipitate was recrystallized from hot ethyl alcohol, and then dried.

TABLE 2

Property	$[Mn(Pyr)_2](CNS)_2$	$[Co(Pyr)_2](CNS)_2$	$[Ni(Pyr)_2](CNS)_2$
Crystal color.....	White with pale greenish tint	Lilac-colored	Light green
Solubility in water at 15°.....	0.14 g in 100 ml	0.146 g in 100 ml	0.065 g in 100 ml
Solubility in C_2H_5OH	0.11 g in 100 ml	0.104 g in 100 ml	0.122 g in 100 ml
Solubility in $(C_2H_5)_2O$.....	0.038 g in 100 ml	0.05 g in 100 ml	Insoluble
Behavior of saturated solutions of the substances with H_2SO_4 and HNO_3.....	No change	Adding the acids to saturated solutions of the substance turns them pink in color	No change
Behavior of saturated solutions of the substances with $AgNO_3$ (0.1 N)	A weak suspension of AgCNS is formed within 0.5 minute; the solution turns violet, the color disappearing after some time.		
Behavior with dilute solution of HNO_3.....	A heavier precipitate of AgCNS; no violet color is apparent		
Behavior with dilute solution of $FeCl_3$	Cherry-red color – the thiocyanogen ion is present.	At first pyramidon is found to be present.	Violet coloring – an excess produces a cherry color.
Behavior of the dry substance when heated in a capillary	Fuses at 176° to a transparent liquid. Turns brown as heating is continued.	Decomposition sets in at 160°.	Decomposes at 210°. A dark brown liquid at 231°.
Electrical conductivity at 15°.....	$\mu_{1000} = 218$; $\mu_{2000} = 241$.	$\mu_{1000} = 214$; $\mu_{2000} = 230$	$\mu_{1000} = 197$; $\mu_{2000} = 199$.
Appearance of the crystals under the microscope.....	Fig. 4	Fig. 5	Fig. 6

Quantitative determination of the Cl yielded the following results:

Taken: 0.1916 g substance: obtained: 0.1082 g AgCl.
Taken: 0.2468 g substance: obtained: 0.1402 g AgCl.
Found %. Cl 13.97, 14.05.

For $[Hg(Pyr)Cl_2]$ (mol. wt. = 502.81), the calculated Cl was 14.1%.

Synthesis of Pyramidon Bromides

Synthesis of dipyramidoncadmium bromide. About 100 ml of a hot solution of pyramidon, saturated at room temperature, was added to 50 ml of a hot 2 N solution of cadmium bromide, $CdBr_2 \cdot 4H_2O$. After washing and recrystallization, the substance was dried at 110° and its Br content determined.

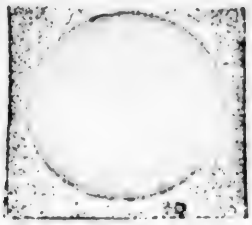


Fig. 1. Crystals of $[Zn(Pyr)_2](CNS)_2$ (x 120).

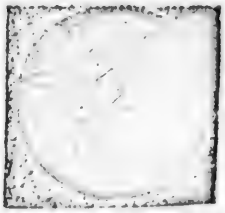


Fig. 2. Crystals of $[Cd(Pyr)_2](CNS)_2$ (x 120).

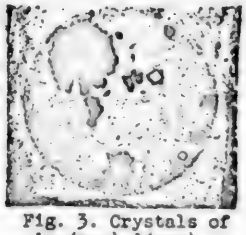


Fig. 3. Crystals of $[Fe(Pyr)_2](CNS)_2$ (x 120).

Fig. 4. Crystals of $[Mn(Pyr)_2](CNS)_2$ (x 120).

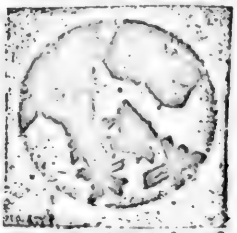


Fig. 5. Crystals of $[Co(Pyr)_2](CNS)_2$ (x 120).

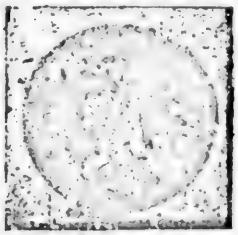


Fig. 6. Crystals of $[Ni(Pyr)_2](CNS)_2$ (x 120)

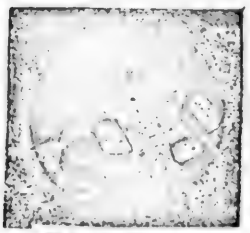


Fig. 7. Crystals of $[Zn(Pyr)]Cl_2$ (x 120).

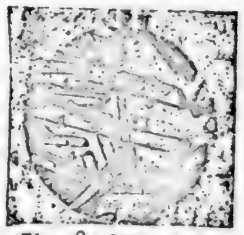


Fig. 8. Crystals of $[Cd(Pyr)_2]Cl_2$ (x 120).

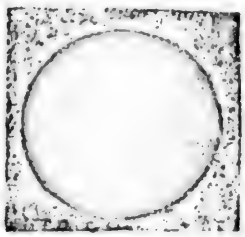


Fig. 9. Crystals of $[Hg(Pyr)]Cl_2$ (x 120).

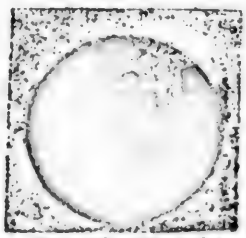


Fig. 10. Crystals of $[Zn(Pyr)]Br_2$ (x 120).

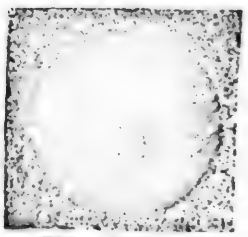


Fig. 11. Crystals of $[Cd(Pyr)_2]Br_2$ (x 120).

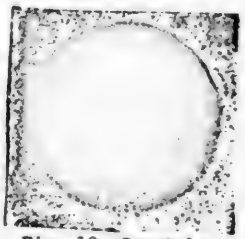


Fig. 12. Crystals of $[Hg(Pyr)]Br_2$ (x 120

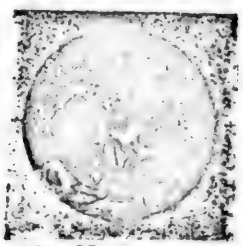


Fig. 13. Crystals of $[Zn(Pyr)]I_2$ (x 120)

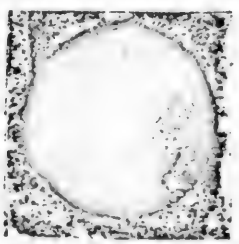


Fig. 14. Crystals of $[Cd(Pyr)]I_2$ (x 120).

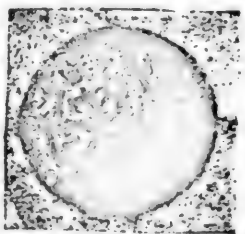


Fig. 15. Crystals of $[Hg(Pyr)]I_2$ (x 120).

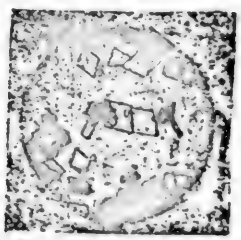


Fig. 16. Crystals of $[Ni(Pyr)_2]I_2 \cdot H_2O$, (x 120).

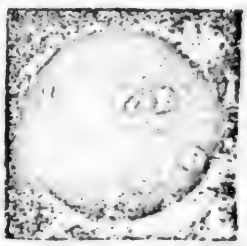


Fig. 17. Crystals of $[Co(Pyr)_2]I_2 \cdot H_2O$ (x 120).

TABLE 3

Property	$[Zn(Pyr)]Cl_2$	$[Cd(Pyr)_2]Cl_2$	$[Hg(Pyr)Cl_2]$
Color.....	White	White	White
Solubility in water at 15°.....	1.49 g in 100 ml.	1.2 g in 100 ml.	0.05 g in 100 ml.
Solubility in C_2H_5OH.....	0.29 g in 100 ml.	0.192 g in 100 ml.	0.1 g in 100 ml.
Solubility in $(C_2H_5)_2O$.....	0.042 g in 100 ml.	0.01 g in 100 ml.	0.06 g in 100 ml.
Behavior of saturated solutions of the substances with cold HNO_3 and H_2SO_4.....	No changes	No changes	No changes
Behavior of saturated solutions with NaOH in the cold.....	At first a precipitate of $Zn(OH)_2$ is formed; it vanishes later with the addition of NaOH in excess.	$Cd(OH)_2 \cdot NH_4OH$ is formed, yielding a precipitate of $Cd(OH)_2$, which is soluble in an excess of the reagent.	Very faint yellow coloring of the solution.
Behavior of saturated solutions of the substances with $AgNO_3$ in the cold.....	A precipitate of AgCl is formed. As more $AgNO_3$ is added, a violet coloring appears — pyramidon is present.		Slight opalescence.
Behavior of saturated solutions of the substances with $FeCl_3$ (dilute).....	Viclet coloring -- pyramidon is present		Slight violet coloring, which quickly vanishes.
Behavior of the dry substance when heated in a capillary.....	Fuses at 216°.	Turns dark at 176°, decomposing as heating progresses.	Turns red at 145°, fuses at 165°, turning into a red liquid.
Electrical conductivity at 15°....	$\mu_{1000} = 236.5$; $\mu_{2000} = 242$.	$\mu_{1000} = 222$; $\mu_{2000} = 239$.	Determination impossible, due to low solubility.
Appearance of crystals under the microscope...	Fig. 7.	Fig. 8.	Fig. 9.

TABLE 4

Property	$[Zn(Pyr)]Br_2$	$[Cd(Pyr)_2]Br_2$	$[Hg(Pyr)Br_2]$
Crystal color....	White	White	White
Solubility in water at 15°....	1.24 g in 100 ml.	0.27 g in 100 ml.	0.04 g in 100 ml.
Solubility in C_2H_5OH.....	0.382 g in 100 ml.	0.204 g in 100 ml.	0.4 g in 100 ml.
Solubility in $(C_2H_5)_2O$.....	0.122 g in 100 ml.	0.05 g in 100 ml.	0.01 g in 100 ml.
Behavior of saturated solutions of the substances with H_2SO_4 and HNO_3 (diluted in the cold.....	No changes. Concentrated solutions cause decomposition, with the liberation of bromine.	No changes.	No changes, owing to its slight solubility in water.
Behavior with NaOH in the cold	A precipitate of $Zn(OH)_2$ is formed, which is soluble in an excess of NaOH.	A precipitate of $Cd(OH)_2$ is formed. The precipitate dissolves when acted upon by NH_4OH.	No changes.
Behavior with $AgNO_3$ in the cold.....	A precipitate of AgBr is formed, and the solution turns violet — pyramidon is present.		Slight opalescence.
Behavior with $FeCl_3$ (dilute)..	Solution turns violet — pyramidon is present.		No changes.
Behavior of the dry substance when heated in a capillary.....	Fuses at 235°, with partial decomposition.	Fuses at 175°.	Decomposes when heated.
Electrical conductivity at 15°.....	$\mu_{1000} = 225$; $\mu_{2000} = 239$.	$\mu_{1000} = 209$; $\mu_{2000} = 227$.	Determination impossible, owing to low solubility.
Appearance of crystals under microscope.....	Fig. 10.	Fig. 11.	Fig. 12.

Taken: 0.1816 g substance: obtained: 0.0940 g AgBr.
Taken: 0.1818 g substance: obtained: 0.0940 g AgBr.
Found %: Br 22.03, 22.

For $[Cd(Pyr)_2]Br_2$ (mol. wt. = 734.82), the computed Br was 21.75%.

Pyramidonzinc bromide was produced in an almost identical manner. Quantitative determination of the Br in the synthesized substance yielded the following results:

Taken: 0.1670 g substance; obtained: 0.1390 g AgBr.
Taken: 0.1818 g substance; obtained: 0.1502 g AgBr.
Found %: Br 35.42, 35.16.

For $[Zn(Pyr)]Br_2$ (mol. wt. = 456.5), the computed Br was 35.01%.

Synthesis of pyramidonmercury dibromide. 10 ml of an alcoholic solution of pyramidon (11.6:100) was added to 25 ml of an alcoholic solution of mercury bromide [2], saturated at 18°, containing approximately 2.5 g of substance. A precipitate formed at once; it was filtered out, washed repeatedly with alcohol, and dried.

Taken 0.1486 g substance; obtained: 0.0932 g AgBr.
Taken 0.1170 g substance; obtained: 0.0746 g AgBr.
Found %: Br 26.69, 27.13.

For $[Hg(Pyr)Br_2]$ (mol. wt. = 591.74), the computed Br was 27.01%.

Pyramidonmercury dibromide may also be synthesized from saturated aqueous solutions of mercury bromide [2] and pyramidon.

See Tables 3 and 4 for the properties of the foregoing compounds.

In conclusion, let us cite the synthesis of a few pyramidon iodides.

Synthesis of pyramidonzinc iodide. A hot solution of pyramidon, saturated at room temperature, was added to a freshly prepared and slightly warmed solution of zinc iodide until no more precipitate formed.

After the substance had been washed, recrystallized, and dried at 70°, the substance was analyzed for I.

Taken 0.2370 g substance; obtained: 0.2030 g AgI.
Found %: I 46.31%.

For $[Zn(Pyr)]I_2$ (mol. wt. = 550.1), the computed I was 46.11%.

Synthesis of pyramidoncadmium iodide. An equal volume of a hot solution of pyramidon (saturated at room temperature) was gradually added to a 0.2 N solution of cadmium iodide, saturated when boiling and containing about 3.7 g of the substance in 100 ml of water. The precipitate was recrystallized and analyzed.

Taken: 0.2400 g substance; obtained: 0.1890 g AgI.
Taken: 0.3068 g substance; obtained: 0.2406 g AgI.
Found %: I 42.57, 42.39.

For $[Cd(Pyr)]I_2$ (mol. wt. = 597.54), the computed I was 42.48%.

Synthesis of pyramidonmercury diiodide. 2.5 g of pyramidon was dissolved in 50 ml of ethyl alcohol, and about 5 g of mercuric iodide was added to the solution. The whole was heated to boiling, and then the excess mercuric iodide was filtered out. After cooling, the precipitate that formed was recyrstallized from a hot alcoholic solution and dried at 80°. Quantitative determination of the Hg as HgS yielded the following results:

Taken: 0.2056 g substance; obtained: 0.0722 g HgS.
Found %: Hg 30.25%.

For $[Hg(Pyr)]I_2$ (mol. wt. = 685.74), the computed Hg was 29.5%.

The properties of the compounds synthesized are given in Table 5.

Besides the foregoing compounds, we also synthesized the pyramidon iodides of nickel and cobalt.

$[Ni(Pyr)_2]I_2 \cdot H_2O$ consists of greenish crystals, which are readily soluble in water and in alcohol. Quantitative determination of I yielded the following results.

Taken 0.1784 g substance; obtained 0.1048 g AgI.
Taken 0.2008 g substance; obtained 0.1178 g AgI.
Found %: I 31.76, 31.72.

The computed I according to the formula above (mol. wt. = 793.11), was 32%.

TABLE 3

Property	$[Zn(Pyr)]I_2$	$[Cd(Pyr)]I_2$	$[Hg(Pyr)]I_2$
Crystal color....	White	White	Pale yellow
Solubility in water at 15°....	3.75 g in 100 ml, yielding a slightly cloudy solution.	0.14 g in 100 ml.	Almost insoluble.
Solubility in C_2H_5OH.....	0.462 g in 100 ml.	0.23 g in 100 ml.	0.48 g in 100 ml.
Solubility in $(C_2H_5)_2O$.....	0.116 g in 100 ml.	0.046 g in 100 ml.	Insoluble.
Behavior of saturated solutions of the substances with H_2SO_4 and HNO_3.....	Dilute acids are without effect; concentrated acids turn the solutions yellow — free iodine is liberated.		Suffers no change, due to the slight solubility of the substance.
Behavior with a NaOH solution in the cold.....	A precipitate of $Zn(OH)_2$ is formed, soluble in an excess of NaOH.	Negligible precipitate.	Suffers no change.
Behavior with a $AgNO_3$ solution..	A precipitate of AgI is formed, and the solution turns violet — pyramidon is present.		Suffers no change.
Behavior with a $FeCl_3$ solution (dilute).....	Reddish-brown flakes are formed.	Violet coloring — pyramidon is present.	No changes.
Behavior of the dry substance when heated in a capillary.....	Darkens at 235°; fuses at 240°, with partial decomposition.	Fuses at 228°, with decomposition.	Decomposes.
Electrical conductivity at 15°	$\mu_{1000} = 239$; $\mu_{2000} = 224$.	$\mu_{1000} = 203$; $\mu_{2000} = 230$.	Determination impossible, owing to its low solubility.
Appearance of crystals under micro.	Fig. 13.	Fig. 14.	Fig. 15

$[Co(Pyr)_2]I_2 \cdot H_2O$, a substance in the form of lilac-red crystals, changes color, turning violet, when carefully heated in the dry state. The substance is readily soluble in water. The I was found to equal 32%. The I computed from the formula = 32%.

Both of these compounds were synthesized by substituting the iodine ion for the chlorine ion in cobalt and nickel chlorides, respectively, by reacting them with an excess of potassium iodide in the presence of pyramidon.

Lastly, we may state that study of the molecular conductivity of the synthesized coordination compounds indicates that they are ternary electrolytes, i.e., they break down into 3 ions. The coordination compounds of pyramidon with mercury are exceptions, as they are only slightly soluble in water and are nonelectrolytes.

It should be noted that zinc, with the sole exception of $[Zn(Pyr)_2](CNS)_2$, coordinates only one molecule of pyramidon, i.e., its coordination number is two,

and not four. Similar compounds have been described in the literature: G. Spacu and R. Ripan [3], for instance, precipitate zinc as $[Zn(Pyr)_2](CNS)_2$, two molecules of pyridine occupying the coordinated positions. Cadmium exhibits the same anomaly in the compound $[Cd(Pyr)]I_2$.

In the case of bivalent mercury we find coordination compounds with pyramidon with the general formula $[Hg(Pyr)X_2]$, where X = Cl, Br, or I; its coordination number is four.

As for the solubility of the synthesized substances, it is found that the mercury compounds and dipyramidonnickel thiocyanate are least soluble; moreover, the solubility of the chlorides, bromides, and iodides of zinc, cadmium, and mercury not only drops because of the increase in the atomic weight of the central atom, but also drops in the following anion sequence: chlorine, bromine, iodine, and thiocyanogen. $[Zn(Pyr)]I_2$, whose solubility is rather high, is the sole exception.

SUMMARY

1. In a neutral medium pyramidon can be introduced into the molecules of the chlorides, bromides, iodides, and thiocyanates of bivalent metals, compounds with the following general formula:

$$[Me(Pyr)_2]X_2 \quad \text{or} \quad [Me(Pyr)]X_2,$$

being formed.

2. These compounds can be synthesized either by the direct action of pyramidon upon salts of the bivalent metals or by a double exchange reaction between two salts in the presence of pyramidon.

3. Seventeen new coordination compounds of pyramidon with bivalent metals have been synthesized and their properties investigated.

4. It is probable that pyramidon may yield similar compounds with metals whose valency is a multiple of two. Work on this aspect of the problem is under way.

LITERATURE CITED

[1] D.I.Ryabchikov and E.A.Terentyev, Doklady USSR Acad. Sci., New Series, 1946, v. LI, No. 4.

[2] S.I.Gusev, J. Analytical Chem., 1, 2 (1946).

[3] G. Spacu and R. Ripan, Zbl., IV, 185 (1923); G. Klein and R. Strebinger, loc. cit., 328.

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THE VINYLATION OF GLYCEROL

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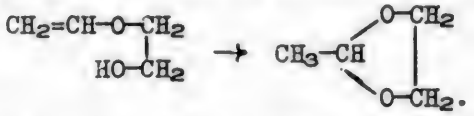
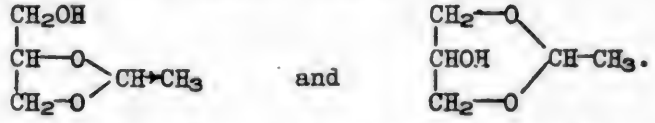
The vinylation of glycerol and the synthesis of the corresponding vinyl ethers are further applications of the A.E.Favorsky and M.F.Shostakovsky reaction [1]. Research on these reactions has been largely confined to the synthesis of vinyl esters of monoatomic aliphatic and aromatic alcohols [2,3]. As for the vinylation of polyatomic alcohols, all we possess are partial statements, chiefly in the patent literature [4]. The latter sources are of a purely orienting nature and, as it later developed, do not give a complete description of the products obtained during the synthesis of glyceryl trivinyl ether. The vinylation of ethylene glycol is a less complicated reaction [5]. The reaction of ethylene glycol with acetylene in an alkaline medium results in the synthesis of monovinyl and divinyl ethers of ethylene glycol, together with a cyclization product and a monovinyl ether, formed in accordance with the following diagram:



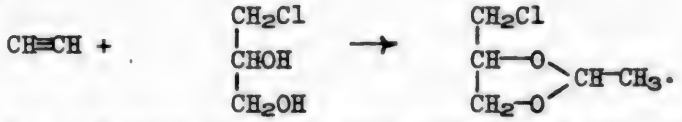
It was highly probable that reacting acetylene with glycerol under the conditions of the Favorsky-Shostakovsky reaction would result in the formation of complete and partial vinyl ethers of glycerol. The latter, in turn, may also cyclize.

The research done by Nieuwland, Hill, and Hibbert [6,7] showed that the reaction of glycerol with acetylene in an acid medium yields nothing but cyclic acetals of glycerol in two isomeric forms:



Both of these forms have been isolated, and their structure has been proved by benzoylating the free hydroxyl group.

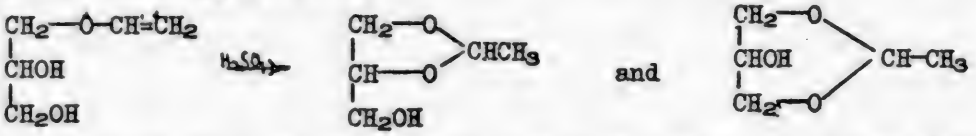
When acetylene is reacted with glycerol monochlorohydrin under these conditions, it is probable that only one acetal is formed; this has been confirmed experimentally [4]:



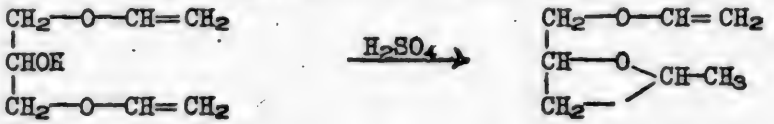
Reviewing all the work that has been done on the synthesis of acetals of the foregoing structure, we must point out that what is common to all of them is the

presence of acid catalysts, which bring about the cyclization of the incomplete vinyl ethers that are formed. Though the incomplete vinyl ethers were conjectured in the papers cited as explanations of the cyclization, we have demonstrated this isomerization clearly by their rearrangement into acetals under the action of traces of sulfuric acid. There can be no doubt of the reality of the cyclization of incomplete vinyl ethers of glycerol in accordance with the foregoing diagrams, for we began with isolated and identified products of the vinylation of glycerol in synthesizing these acetals.

Cyclization of glycerol monovinyl ether results in the synthesis of two isomeric acetals of the following structure:

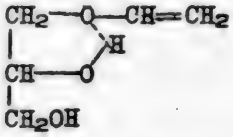


When the 1,3-divinyl ether of glycerol is cyclized, only one acetal is formed:

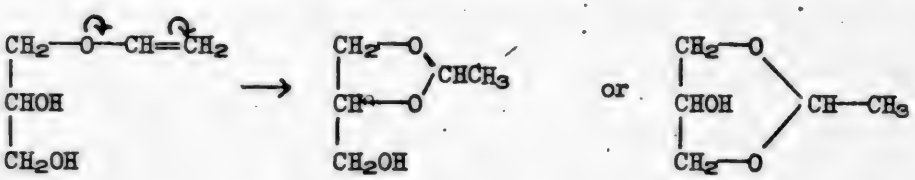


This process of the isomerization of the incomplete vinyl ethers of glycerol cannot take place under the conditions of vinylation in an alkaline medium, but we find that cyclic acetals are formed during the fractionation of the reaction products. The incomplete vinyl ethers of glycerol isolated by us proved to be quite stable against the action of alkalies, even at high temperatures. The weightiest argument against the formation of glycerol acetals in an alkaline medium during the glycerol's vinylation is the high yield of glyceryl trivinyl ether. When an excess of acetylene is present, the glycerol is completely vinylated.

The formation of acetals or the cyclization of incomplete vinyl ethers is hindered under normal conditions by the appearance of an intramolecular hydrogen bond:



Establishment of an intramolecular hydrogen bond takes place at moderate temperatures, the bond dissociating when heated, the electron cloud being displaced, i.e., we have a tautomeric effect. This tautomeric effect activates the bond of the vinyl radical, which causes the hydroxyl proton to attach itself to the β-carbon atom; at the same time a bond is established between the α-carbon atom and the oxygen:



We find a similar process of acetal formation in the interaction between vinyl alkyl ethers and monoatomic alcohols [8,9].

The vinylation of glycerol is a complex reaction, which enables one to

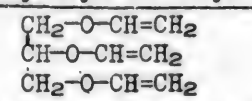
synthesize a number of interesting andlittle-known compounds, depending upon the reaction conditions.

The structure of the products of glycerol vinylation was proved by hydrolyzing them in an acid medium and then determining the acetic anhydride and other constituents of the vinyl ethers or their acetals by the usual methods [11]. As for the incomplete vinyl ethers of glycerol, their structure was established by the hydrogenation, in addition to hydrolysis.

It should also be borne in mind that thenotion of the structure of the vinyl ethers of glycerol stems from the very process of their synthesis. In particular, the formation of glyceryl trivinyl ether takes place as follows:

EXPERIMENTAL

1. Glyceryl Trivinyl Ether



200 g of chemically pure glycerol and 20 g of powdered potassium hydroxide were placed in a rotating 3-liter autoclave (fitted with a monometer and a thermometer). Acetylene was fed into the autoclave from a tank until the internal pressure reached 10 atm. Then the autoclave's rotating mechanism was started, and the autoclave was heated to 180-190°. The course of the reaction was checked by the manometer and thermometer readings.

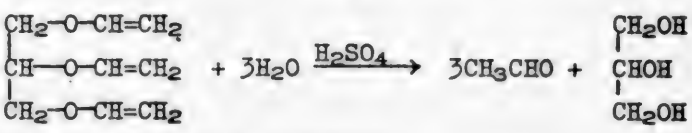
The acetylene is absorbed very quickly at first, as is indicated by the pressure drop within the autoclave, the heating and the increase in temperature continuing. After the acetylene had been absorbed, the autoclave was cooled, and acetylene was again forced into the autoclave as outlined above. Acetylene was thus added 12 times, until the absorption of the acetylene practically stopped.* The vinylation product taken from the autoclave was dried with potash and then fractionated. Fractionation yielded 298 g of glyceryl trivinyl ether, with a b.p. of 164-165° (760 mm), or a yield that was 90.3% of theory.

d_4^{20} 1.0335; n_D^{20} 1.4381; MR_D 46.75,
$C_9H_{14}O_3$ F 3. Calculated; MR_D 47.29.

0.144 g substance: 12 g benzene: Δt 0.37.
0.152 g substance: 12 g benzene: Δt 0.39.
Found: M 167.0, 166.2.

$C_9H_{14}O_3$. Calculated: M 170.
11.55 mg substance: 8.88 mg H_2O; 20.71 mg CO_2.
10.52 mg substance: 8.32 mg H_2O; 18.85 mg CO_2.
Found %: C 63.42, 63.12; H 8.86, 8.60.
$C_9H_{14}O_3$. Calculated %: C 63.53; H 8.23.

Hydrolysis of glyceryl trivinyl ether. The glyceryl trivinyl ether was hydrolyzed as follows:



*Under the reaction conditions part of the acetylene polymerizes.

For this hydrolysis reaction we took freshly distilled glyceryl trivinyl ether, with the constants given above. 60 ml of a 0.2 N solution of sodium bisulphite, 0.078 g of the ether, and 30 ml of a 5% solution of sulfuric acid were placed in a 250-ml Erlenmeyer flask fitted with a ground-glass stopper.

The mixture was shaken for 25-30 minutes. Then the reaction mixture was kept for another 15-20 minutes, and a 0.5% solution of starch was added (as an indicator). The excess sodium bisulfite was titrated back with 0.1 N iodine solution. Each titration was run together with a blank test. The titration results are given below.

0.078 g of the substance required 19.9 ml of iodine solution. T = 0.01279.

The percentage of acetaldehyde found was 93.2% of theory.

2. Synthesis of the Mono- and 1,3-Divinyl Ethers of Glycerol

The reaction was carried out under conditions that differed from those above in order to obtain a closer insight into the reaction mechanism of the vinylation of glycerol.

These experiments were made with the same quantities of glycerol and potassium hydroxide and at the same temperature of 180-190°, but in this test series only 50% of the acetylene required for complete vinylation was used. This resulted in a mixture of complete and incomplete vinyl ethers of glycerol.

The mixture yielded the following fractions: 1) b.p. 58° (7 mm); 2) b.p. 82-84° (7 mm); 3) b.p. 128-130° (6 mm); and 4) b.p. 180-182° (760 mm).

The substance with a b.p. of 58° (7 mm), and 164-165° (760 mm), d_4^{20} 1.0335 and n_D^{20} 1.4381 is glyceryl trivinyl ether.

Only an extremely small amount of the 83-84° (7 mm) fraction was recovered; it had the following constants:

d_4^{20} 1.0521; n_D^{20} 1.4430; MR_D 36.8.

$C_7H_{12}O_3$. Calculated: MR_D 37.3.

0.327 g substance; 17.5 g benzene: Δ t 0.70.
0.231 g substance; 14.4 g benzene: Δ t 0.62.
Found: M 143.1, 146.
$C_7H_{12}O_3$. Calculated: M 144.

8.58 mg substance: 18.12 mg CO_2; 6.17 mg H_2O.
8.60 mg substance: 18.22 mg CO_2; 6.14 mg H_2O.
Found %: C 57.87, 57.60; H 8.06, 7.99.
$C_7H_{12}O_3$. Calculated %: C 58.10; H 8.31.

Thus the 83-84° (7 mm) fraction is the glyceryl 1,3-divinyl ether.

Hydrolysis of glyceryl divinyl ether. The glyceryl divinyl ether was hydrolyzed under the conditions set forth above in order to prove its structure.

0.111 g of the substance required 15.6 ml of iodine solution. T = 0.01279.

The percentage of acetaldehyde found was 83% of theory.

Hydrogenation of glyceryl divinyl ether in the presence of Rainey nickel. The

Rainey nickel [10] was prepared from a 1:1 melt of nickel and aluminum, by treating it with a solution of caustic soda until all the aluminum had been removed. The hydrogen was obtained electrolytically and was passed through solutions of alkali, permanganate, pyrogallol, and strong sulfuric acid.

Freshly prepared 1,3-divinyl ether of glycerol with the following constants: b.p. 83-84° (7 mm); d_4^{20} 1.0521; n_D^{20} 1.4430.

Hydrogenation was effected at room temperature in a closed vessel, which was agitated horizontally. The hydrogen was fed into the vessel from a gas tank.

We used 7 g of the divinyl ether, 30 ml of ethyl alcohol, and about 2 g of the nickel catalyst in the hydrogenation reaction. During the course of 3 hours 0.96 liter of hydrogen was absorbed, i.e. 0.12 liter less than required by theory. The alcohol was driven off from the reaction mixture in vacuum. The residue remaining after the alcohol had been driven off was fractionated in vacuum and then redistilled at atmospheric pressure.

The hydrogenation product had the following constants: b.p. 191-192°; d_4^{20} 0.9221.

The literature gives the following data [12] for the α,α'-diethyl ether of glycerol: b.p. 190-191°; d_4^{20} 0.920.

We may conclude from these hydrogenation results that in the glyceryl divinyl ether the vinyl groups are located at the 1,3 positions, which agrees with the reaction diagram given above.

Analysis of the 128-130° (6 mm) fraction showed that the substance had the following constants:

d_4^{20} 1.1283; n_D^{20} 1.4521; MR_D 29.4

$C_5H_{10}O_3$. Calculated MR_D 29.12.

0.110 g substance: 17 g benzene: Δt 0.27.
0.130 g substance: 13.5 g benzene: Δt 0.41.
Found: M 120.2, 119.8.
$C_5H_{10}O_3$. Calculated: M 118.

7.980 mg substance: 6.216 mg H_2O; 14.568 mg CO_2.
5.518 mg substance: 4.010 mg H_2O; 9.570 mg CO_2.
Found %: C 50.02, 49.79; H 8.72, 8.60.
$C_5H_{10}O_3$. Calculated %: C 50.5; H 8.3.

The constants for the 128-130° (6 mm) fraction correspond to glyceryl monovinyl ether.

Hydrolysis of glyceryl monovinyl ether. Hydrolysis by the method adopted by us was used to prove the structure of the glyceryl monovinyl ether.

0.090 g of the substance required 5.4 ml of iodine solution. T = 0.01279.

The percentage of acetaldehyde found was 94.8% of theory.

Hydrogenation of glyceryl monovinyl ether in the presence of Rainey nickel. Freshly prepared glyceryl monovinyl ether, with the following constants: b.p. 128-130° (6 mm); d_4^{20} 1.1283; n_D^{20} 1.4521, was used for hydrogenation.

Hydrogenation was effected in a closed vessel under the conditions set forth above.

We used 9 g of glyceryl monovinyl ether, 30 ml of ethyl alcohol, and about 2 g of the nickel catalyst for the reaction.

In the course of 4 hours 1.4 liters of hydrogen was absorbed instead of the

1.7 liters required by theory. After the alcohol had been driven off, the residue was repeatedly distilled in vacuum and at atmospheric pressure.

The hydrogenation product possessed the following constants: b.p. 230-236°; n_D^{20} 1.4282.

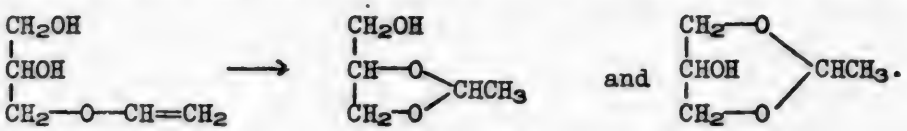
Data in the literature [12]: the α-ethyl ether of glycerol has a b.p. of 225-230°.

Comparison of the boiling point of the substance prepared by hydrogenating glyceryl monovinyl ether with that of the α-ethyl ether of glycerol indicates that they are rather close together.

In the monovinyl ether it is apparent that the vinyl group occupies the α position.

3. Cyclization of Incomplete Vinyl Ethers

a) Cyclization of Glyceryl Monovinyl Ether When Heated With Traces of Acid



7 g of the monovinyl ether was placed in a small flask fitted with a herringbone dephlegmator and then fractionated in vacuum over Wood's metal. The third fractionation yielded 5.4 g of a mixture of isomers. A tarry residue remained in the flask.

Cyclization of the monovinyl ether at room temperature in the presence of traces of HCl was accompanied by a warming up of the reaction mixture.

The constants of the cyclic 1,2-acetal were found to be: b.p. 97-99° (9 mm); d_4^{20} 1.1304; n_D^{20} 1.4441.

The literature gives the following data for the cyclic 1,2-acetal [7]: b.p. 70° (1 mm); d_4^{17} 1.1243; n_D^{17} 1.4415.

b) Cyclization of the 1,3-Divinyl Ether of Glycerol When Heated With Traces of Acid

5 g of the 1,3-divinyl ether of glycerol was placed in a small flask connected to a herringbone dephlegmator and then fractionated in vacuum over Wood's metal. The first fractionation yielded 3.4 g of the cyclic acetal of the 1,3-divinyl ether of glycerol.

The isomerization of the divinyl ether at room temperature in the presence of traces of hydrochloric acid is accompanied by a warming up of the reaction mixture.

The cyclic acetal synthesized possessed the following constants: b.p. 75-76° (9 mm); d_4^{20} 1.0790; n_D^{20} 1.4397.

SUMMARY

1. The vinylation of glycerol at a temperature of 180-190° with an excess of acetylene (exhaustive vinylation) in the presence of 10% KOH results in the syn-

synthesis of glyceryl trivinyl ether with a yield of 90% of theory.

2. Vinylation at 180-190° with not enough acetylene present results in the synthesis of the complete glyceryl ether as well as the formation of incomplete vinyl ethers, though in extremely minute quantities.

3. In an alkaline medium the mono- and 1,3-divinyl ethers of glycerol are stable, but fractionation of the vinylation products from the reaction mixture has established that the mono- and 1,3-divinyl ethers of glycerol are cyclized, forming the corresponding cyclic acetals. The isomerization of incomplete glyceryl vinyl ethers is catalyzed by the hydrogen ion.

4. The mechanism of the cyclization of incomplete glyceryl vinyl ethers during the formation of cyclic acetals boils down to the formation of a hydrogen bond between the oxygen of the initial vinyl ether and the hydrogen of the mineral acid, an intramolecular hydrogen bond being established when no such acid is present.

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THE CHEMISTRY OF THE XANTHATES AND VISCOSE

IV. VISCOSE COMPONENTS THAT ADD AND SPLIT OFF A SULFUR ATOM. OXIDATIVE-REDUCING ADDITION OF SULFUR

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GENERAL INTRODUCTION

1. Composition of Viscose

Viscose, which is characterized by a complex constitution that changes continuously as it ripens, contains various sulfur-containing substances in an aqueous alkaline medium (sodium hydroxide and soda). Of these, the most typical of viscose are cellulose xanthate and sodium trithiocarbonate. As we know, the degree of substitution and the distribution of the dithio groups in cellulose xanthates produced by the action of carbon disulfide upon alkali cellulose are quite diverse, depending upon the quantity of carbon disulfide used, the conditions under which the cellulose is xanthated, and the time the viscose is stored.

Cellulose xanthates, the composition of which may be represented by the general formula $\left[C_6H_{10-x}O_{5-x}\left(OC\overset{S}{\underset{SNa}{}}\right)_x\right]_n$, are, chemically speaking, a heterogeneous mixture of substances that differ in the number and location of the dithiocarbonate groups within the molecule. Moreover, it is self-evident that samples of commercial cellulose molecules have different molecular weights, to judge by their fractionating separation from solutions, their varying viscosities, etc. (even when their ash content and impurities are more or less constant values), not to mention the fact that some glucose groups may be partially oxidized.

The surface xanthation of the hypothetical micelles, assumed but not proved by Lieser [1] and other chemists, cannot be taken as the main reason for the chemical heterogeneity of cellulose xanthates. In fact, the sulfidation and the replacement of the hydroxyl groups in the individual glucose groups may not be the same at all depths within the fiber, partly because of the retarded diffusion of the reagents into the fiber, especially in regenerated cellulose. The old notions: that cellulose xanthates have a definite composition, say, the composition of a monocellulose xanthate [2] at the beginning, or that of a dicellulose xanthate [3], or again, a monoglucane xanthate or a diglucane xanthate [4], and that as the viscose ripens the cellulose "polymer" grows, have been rejected; in reality, what occurs is the hydrolytic splitting off of dithiocarbonate groups from the glucose residues and the redistribution of the sulfur within the viscose substances.

The colloido-chemical heterogeneity of the xanthates and the gradual coagulation of the viscose are consequences of the chemical heterogeneity and low chemical stability of the xanthates and the changes in the composition of the viscose. Among the transformations of the xanthates and the substances containing sulfur in viscose, the oxidative transformation effected by atmospheric oxygen, discussed in our previous article [5] is of more than ordinary importance.

As early as the end of 1934, our laboratory was engaged in a study of the

oxidative transformation of ethyl xanthate to diethyl xanthate by the action of the air. In one of our papers [8] it was pointed out that the formation of cellulose dixanthide when a commercial xanthate and viscose were oxidized by the air ought to accelerate the ripening of the viscose, owing to the instability of dixanthides in an alkaline medium.

As a rule, the dithiocarbonate groups that split off from xanthates during the ripening of viscose do not liberate free carbon disulfide and caustic soda, as is assumed by Geiger [7], for example (this might occur to a greater extent upon heating), but are converted into various sulfur-containing substances, some of the latter being formed even during the xanthation of alkali cellulose. Various oxidative-reducing, hydrolytic, and oxidative transformations, accompanied by colloidochemical phenomena, take place during the ripening of viscose, especially when atmospheric oxygen is present.

A trithiocarbonate is synthesized in the xanthation of alkali cellulose, about 25% of the carbon disulfide employed in xanthating the alkali cellulose being used in its formation under ordinary conditions. As the viscose ripens, the quantity of sodium trithiocarbonate increases, though part of it undergoes hydrolytic and oxidative conversions. The problem of the other sulfur compounds in viscose is less clear.

As long ago as 1824 Zeise noticed that carbon disulfide reacts with dissolved sulfides, and somehwat later Berzelius [8] explained this as the formation of sulfur derivatives of the carbonates (trithiocarbonates) in accordance with the equation:

$$CS_2+Na_2S=Na_2CS_3$$

The trithiocarbonates of sodium and other metals were also prepared by a different method at the beginning of the last century, namely: by the action of carbon disulfide upon sodium hydroxide. This reaction was pictured in the form of an equation (Berzelius); the latter is only a summary and incomplete picture, however, of the transformations that take place:

$$6NaOH + 3CS_2 = 2Na_2CS_3 + Na_2CO_3 + 3H_2O$$

It was likewise noted that the trithiocarbonate may suffer decomposition upon heating (with partial splitting off of the carbon disulfide and formation of sodium sulfide) as well as hydrolysis, in particular (with the formation of carbonates, and oxidation by atmospheric oxygen), resulting in the accumulation of the disulfide (Na_2S_2) and the thiosulfate ($Na_2S_2O_3$). Berzelius gave the following equation for the hydrolysis of the trithiocarbonate by water:

$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S,$$

sodium sulfide being formed when an alkali was present. This equation is correct for certain specified conditions (Ueoman [9]). A similar hydrolysis takes place in the presence of sodium zincate [10].

Many papers have been devoted at various times to the study of the reaction of sodium hydroxide with carbon disulfide, as well as to the transformations of a trithiocarbonate and alkali sulfides. These researches indicated that viscose must contain sodium sulfide, which forms sodium trithiocarbonate in the presence of free carbon disulfide. For a time the question of whether viscose contained sodium sulfide and whether sodium hydroxide reacted with carbon disulfide was still unsettled.

Kita and Tomihisa [11], for instance, concluded that when carbon disulfide is reacted with a 15% solution of caustic soda, a 3:2 ratio of trithiocarbonate to soda is established, no sodium sulfide being found, although small quantities of sulfur are recovered upon oxidation, its formation being attributable to the presence of polysulfides in the mixture. The presence of free sulfur in the

viscose is also noted by Bernhardt [12].

Tanemura, Kohno, and Miyoshi detected sodium sulfide [13] when they mixed aqueous solutions of carbon disulfide and sodium hydroxide, its quantity varying with the ratio between the reagents. Their tests confirmed the old data on the formation of soda and sodium sulfide when the trithiocarbonate was hydrolyzed, but the source of the formation of these salts was not ascertained.

Geiger [7] again rejected the data on the presence of sodium sulfide in viscose, as he did not get a positive reaction with lead acetate in his experiments. He attributed the formation of the trithiocarbonate and soda when caustic soda is reacted with carbon disulfide to the intermediate formation of salts of dithiocarbonic and monothiocarbonic acids, which remind one of Ragg's diagram [4] for the hydrolytic cleavage of xanthates, resulting in the formation of sodium dithiocarbonate and sodium hydrosulfide, together with soda. In so doing, Geiger complicated the problem of sodium sulfide in viscose still further.

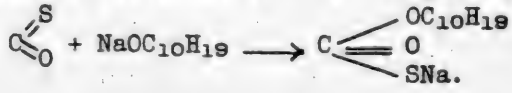
In agreement with Berzelius' long-established assertions, Cross and Bevan held that the trithiocarbonate in viscose is hydrolyzed, forming sodium sulfide and soda [15].

Definite positive data on the presence of sodium sulfide in viscose are contained in the paper by R. S. Neiman, V. A. Kargin, and E. I. Fokina [16], in which the fruitful application of potentiometric methods of analysis to viscose using silver and glass electrodes, is described. The presence of sodium sulfide in viscose was also noted more than once in our laboratory during these same years [17].

The presence of sodium sulfide in viscose gave grounds for assuming equations that expressed the reaction of carbon disulfide with caustic soda at lower carbon disulfide-caustic soda ratios than in the classical equations. In these latter equations, either the sodium sulfide is supposed to be formed together with the trithiocarbonate (Leuchs [18]) or nothing but sodium sulfide is supposed to be formed during the initial phase, it combining with carbon disulfide in the second phase to form the trithiocarbonate (Tanemura [13]).

Though considering the presence of sodium sulfide in viscose proven, we need not suppose that all the trithiocarbonate is synthesized via the sodium sulfide during the xanthation and ripening of the viscose, as indicated by the diagram supported by Tanemura, even if this is the most usual way in which the trithiocarbonate is formed. Likewise, the sodium sulfide need not be formed solely as a result of the reaction of caustic soda with carbon disulfide, but may arise as the result of other transformations.

In considering the methods of formation of sulfur compounds in viscose, we cannot ignore the fact that the initial products of the reaction of carbon disulfide with water, and with alkalies in particular may well be dithiocarbonic acid and its salts. Ultraviolet-light investigations justify the assumption (Hantzch) that dithiocarbonic acid is formed. We have very little information, however, on the mono- and dithiocarbonic acids, nor is their existence in the form of salts proven. The monoesters of dithiocarbonates exist, however, as the usual xanthates of alcohols. The monoester of monothiocarbonic acid is mentioned in the literature as the addition product of carbon disulfide and such alcoholates as menthol, as shown by L. A. Chugayev [19]:



If the patents are to be believed [20], cellulose also yields monothiocarbonic derivatives. But it is known that Cross and Bevan denied the reaction of alkali cellulose with carbon disulfide [15]. Bernhardt considers the existence of carbon oxysulfide in viscose to be probable [12].

A salt of dithiocarbonic acid may be considered the initial product of the reaction of carbon disulfide with alkali; it may also be prepared by the hydrolysis of the trithiocarbonate.

Ragg's paper [14], records the reactions of hydrolytic cleavage of cellulose xanthates by means of caustic soda and sodium hydrosulfide, the reaction products including salts of dithiocarbonic and monocarbonic acids when caustic soda is used. In their papers, Cross and Bevan, the inventors of the viscose process, note that when viscose ripens xanthate groups split off as an acid salt of dithiocarbonic acid, which is immediately cleaved into carbon disulfide and sodium hydroxide according to Heuser [21], for instance, the latter two substances further reacting with each other in the presence of an excess of alkali, forming soda, the trithiocarbonate, and sodium sulfide. The trithiocarbonate is further hydrolyzed, forming soda and sodium sulfide, according to Berzelius. When sodium hydrosulfide acts upon cellulose xanthate the cellulose may be separated out and trithiocarbonate formed. The equations noted down by Ragg were not confirmed by direct experiment, but they are worthy of attention in that the impoverishment of cellulose xanthates in point of its xanthate groups as viscose ripens is quite naturally explainable by reactions of hydrolytic cleavage in an aqueous-alkaline medium.

Ragg indicates the source of the formation of sodium hydrosulfide and, hence, of sodium sulfide and trithiocarbonate, as the xanthate groups of the cellulose.

In the diagrams subsequently published by Geiger, the formation of trithiocarbonate and soda is attributed to the formation of a salt of dithiocarbonic acid, two molecules of which form the trithiocarbonate and a salt of the monothiocarbonic acid, the latter in turn forming soda and the trithiocarbonate by reacting with a molecule of the dithiocarbonic acid. We consider the formation of a salt of dithiocarbonic acid from carbon disulfide and caustic soda to be quite probable, but Geiger's hypothetical double-decomposition reactions between the dithio- and monothiocarbonic acids to be hardly likely in an electrolytic medium, though they may be possible when anhydrous mixtures of salts of the above acids are heated, provided they do not decompose directly, yielding carbon oxysulfide or, to some extent even yielding the initial constituents--carbon disulfide and sodium hydroxide.

It must be thought that in the case of thiocarbonic acids hydrolytic processes must take place with the participation of caustic soda and sodium sulfide or sodium hydrosulfide, and not as a result of direct double decomposition reactions between the thiocarbonic acids themselves. A fundamental defect in Geiger's diagram is his discarding sodium sulfide completely as one of the viscose components. In the absence of an excess of free carbon disulfide to bind the sodium sulfide and form the trithiocarbonate there ought to be sodium sulfide in the viscose, and this is corroborated by analysis of the latter.

The view previously expressed by Heuser and defended by Geiger: that a drop in the degree of cellulose xanthation (raising the "polymer" and lowering the gamma number) during the ripening of viscose depends upon splitting off free carbon disulfide and caustic soda, the carbon disulfide then being redistributed to form xanthate groups and trithiocarbonate cannot be accepted without reservations.

The splitting off of free carbon disulfide from xanthates is not usually

observed; it can take place when a dry xanthate is heated, but not in an alkaline salt viscose medium. Transformations due to hydrolytic conversions of the xanthate groups via salts of dithiocarbonic acid are more likely. Supplementary xanthation of the cellulose xanthates by free carbon disulfide are of very limited importance (Danilov, Rizob [17]), while the splitting off of free carbon disulfide from the xanthate and its partial re-addition to the cellulose are even more unlikely. These reactions can only occur to a very limited extent.

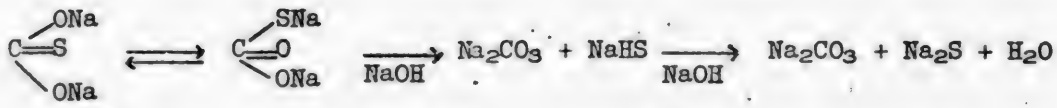
The xanthate recovered after the xanthation of alkali cellulose contains free carbon disulfide, the percentage of which in the viscose gradually decreases.

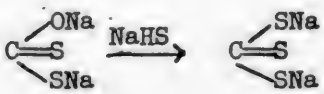
The sources of the thiocarbonate sodium sulfide and soda formed in the viscose are a few reactions, ignoring the fact that soda enters the viscose together with the caustic soda and is produced by the absorption of carbon dioxide from the air.

The reaction of carbon disulfide with caustic soda and of the products of this reaction with one another may be set forth by means of the following diagrams:

(1)

(2)


(3)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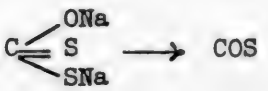
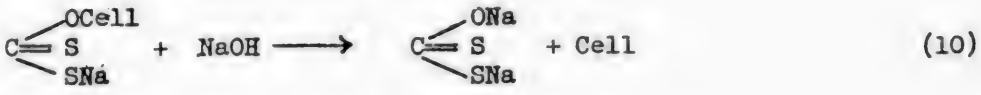

(8)

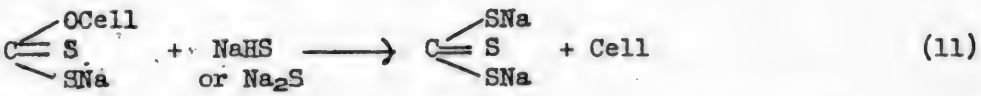
(9)

Sosium sulfide and bisulfide (hydrosulfide) are formed as a result of hydrolytic transformations of salts of dithiocarbonic and monothiocarbonic acids, the trithiocarbonate, and the oxysulfide in the presence of caustic soda (Equations 2,3,5,6,8,9). The trithiocarbonate comes from the dithiocarbonic acid as a result of the latter's reaction with sodium hydrosulfide (Equation 4) or by the reaction between sodium sulfide and carbon disulfide (Equation 7). The dithiocarbonate that serves as the source of the sodium sulfide and the trithiocarbonate

is formed as a result of the reaction of carbon disulfide with caustic soda as well as of the hydrolytic cleavage of the xanthate groups under the action of caustic soda. The action of sodium hydrosulfide upon cellulose xanthate gives rise to the trithiocarbonate. The diagram of these reactions is as follows:



(10)



(11)

These equations of ours are a modification of the Ragg-Heuser diagrams.

In addition to the three indicated sources of the trithiocarbonate (from the dithiocarbonate and the hydrosulfide, from sodium sulfide and carbon disulfide, and as a result of the hydrolysis of the xanthates by sodium hydrosulfide and sodium sulfide), it may also be synthesized from the perthiocarbonate by the action of substances that remove sulfur from the latter.

2. Adding and Detaching Sulfur from the Constituents of Viscose

Major changes and complications in the transformations of the sulfur-containing substances in viscose, beginning with cellulose xanthate, trithiocarbonate, etc., are effected by the oxygen of the air, which is always present in industrial alkali cellulose and acts upon the industrial xanthate and viscose during various stages of production. The composition of viscose is fundamentally affected by the action of oxygen. The action of atmospheric oxygen upon cellulose xanthate gives rise to a dixanthide, as described in our preceding paper. [5] (Danilov and Grad). The sulfur-containing by-products in viscose are easily oxidized by atmospheric oxygen, resulting in an accumulation of oxidation products rich in oxygen and sulfur owing to a simultaneous oxidation and reduction reaction.

Some time ago S. N. Danilov, in discussing the problem of "nitrite" viscose [23] (Moscow Conference on Artificial Fibers, December 1934), pointed out that viscose ought to contain products that are greatly enriched with sulfur, such as: perthiocarbonates and polysulfides. During the intervening years experiments have been carried out in the Laboratory for the Chemical Treatment of Cellulose of the Leningrad Technological Institute on the oxidation of ethyl xanthate to a dixanthide by atmospheric oxygen, which were later extended to other xanthates, including cellulose xanthate, as has been mentioned above.

S. N. Danilov suggested the use of potassium cyanide and sodium sulfite for detecting the products enriched with sulfur, and this procedure was then checked experimentally [22,24]. It was found that potassium thiocyanate and sodium thiosulfate were formed when the cyanide and the sulfite were added to the cellulose; when the potassium cyanide was added to the cellulose, the latter was observed to turn pink, reminding one of the pinkish color of "sulfite" viscose, i.e., a viscose containing added sodium sulfite (to the alkali cellulose or to the viscose). Sodium arsenite acts similarly.

In comparing the role of sodium sulfite in viscose and in cuprammonium solutions, we (S. N. Danilov and E. P. Chilina [25]) pointed out that in cuprammonium solutions this salt is an antioxidant, whereas its role is a dual one in viscose: antioxidant action and, what is particularly important, its action

as an agent that eliminates sulfur from polysulfides and perthiocarbonate (stabilization of viscose).

Below we describe experiments designed to ascertain the constitution of viscose and the discovery within the latter of substances that can supply sulfur to potassium (or sodium) cyanide, sodium sulfite, and sodium arsenite.

Our laboratory was the first to pose the question of the similarity of the action of the foregoing salts upon viscose and to employ the potassium-cyanide method and the addition of other "stabilizers" to establish the composition of viscose and the presence of polysulfide components within it.

Experiments have shown that when viscose is stored (ripened), substances accumulate within it that are able to transfer a sulfur atom to sodium cyanide, sulfite, and arsenite. Substances of this kind are: cellulose dixanthides, sodium perthiocarbonate, sodium disulfide, and, in part, sodium thiosulfate. The percentage of sodium disulfide must rise with oxidation by the air, as part of the sodium sulfide (sodium hydrosulfide) is oxidized to the disulfide:

$$NaHS \xrightarrow{O_2} Na_2S_2 \xrightarrow{O_2} Na_2S_2O_3 \qquad (12)$$

$$Na_2S_2 + CS_2 \longrightarrow \begin{matrix} & SNa \\ C & = S-S \\ & SNa \end{matrix} \qquad (13)$$

The disulfide reacts more readily with carbon disulfide to form the perthiocarbonate than sodium sulfide reacts with it to form the trithiocarbonate as the heat of formation of the perthiocarbonate is higher than the heat of formation of the trithiocarbonate:

$$Na_2S + CS_2 = Na_2CS_3 + 5700 \text{ Large cal.} \qquad (14)$$

$$Na_2S_2 + CS_2 = Na_2CS_4 + 8550 \text{ Large cal.} \qquad (15)$$

As our experiments have shown, the trithiocarbonate can be readily produced from the perthiocarbonate by detaching one atom of sulfur from the latter with sodium cyanide, sulfite, or arsenite. The detaching of an atom of sulfur from the perthiocarbonate by means of potassium cyanide has been pointed out by Ueoman [8] and has been explored by us. What remains to be cleared up is whether sodium trithiocarbonate can detach a sulfur atom from sodium disulfide (Ueoman). It is known that the trithiocarbonate readily converts into the perthiocarbonate in the presence of sulfur. These conversions are accompanied by the evolution of heat:

$$Na_2CS_3 + S = Na_2CS_4 + 4920 \text{ Large cal.} \qquad (16)$$

$$Na_2S_2 + Na_2CS_3 = Na_2CS_4 + Na_2S + 2850 \text{ Large cal.} \qquad (17)$$

The heat effects of the reactions between sodium sulfide and disulfide and carbon disulfide cited above indicate that the perthiocarbonate is more readily formed from sodium disulfide and carbon disulfide than the trithiocarbonate from sodium sulfide and carbon disulfide. These heat values lead us to think that the trithiocarbonate is more readily formed via the perthiocarbonate in the presence of sulfur-detaching substances than by the direct reaction of sodium sulfide with carbon disulfide.

A general conclusion of our investigations is that sodium cyanide, sulfite, and arsenite can act as antioxidant substances in the transformation of viscose

(of which there is no doubt as far as sodium sulfite is concerned), but that their role is especially important as sulfur-removing substances.

Their antioxidant role in viscose can manifest itself in a diminution of the quantities of cellulose dixanthide, sodium perthiocarbonate, sodium disulfide, and sodium thiosulfate. Our experiments have shown that sodium sulfite and sodium arsenite, and potassium cyanide in particular, detach an atom of sulfur from cellulose dixanthide, sodium disulfide, and sodium perthiocarbonate.

Sodium sulfite and arsenite and, especially, sodium cyanide are reagents acting on the polysulfurized products in viscose.

EXPERIMENTAL

1. Collateral Sulfur-Containing Substances in Viscose

Besides the cellulose xanthates, various sulfur compounds, which are multifariously transformed within the viscose, are formed in the xanthation of alkali cellulose and the ripening of viscose. Our laboratory was the first to find a proof of the presence of polysulfurized products within viscose at various periods of ripening under the action of atmospheric oxygen, such as: cellulose dixanthides, sodium disulfide, and sodium perthiocarbonate. The problem of the accumulation of sodium thiosulfate within viscose has been cleared up. The transformations of these substances within viscose are closely bound up with the conversions and the formation of other sulfur-containing substances, namely: sodium sulfide, sodium trithiocarbonate, and sodium sulfite.

Sodium sulfide and disulfide. Sodium sulfide is formed: 1) in the xanthation of alkali cellulose, as a result of the reaction of carbon disulfide with caustic soda; it is found in viscoses that are not very old (about 0.25%); 2) in the hydrolytic cleavage of the trithiocarbonate; 3) from sodium disulfide when acted on by sulfur-removing substances; 4) in the reaction between an alkali and carbon oxysulfide, the presence of which, in viscose, parenthetically, requires confirmation.

Sodium hydrosulfide can be obtained by the hydrolysis of sodium sulfide in the presence of an insufficiency of alkali or, as may be imagined, by the hydrolysis of salts of di- and monothiocarbonic acids by caustic soda.

Sodium disulfide arises from the following sources in viscose: 1) the oxidation of sodium sulfide and, especially, sodium hydrosulfide by oxygen, which was pointed out long ago by Filol [28] and other authors:

$$2NaSH + \tfrac{1}{2}\,O_2 \longrightarrow Na_2S_2 + H_2O;$$

Other authors (S. A. Shschukarev and E. M. Kireyeva-Tuzulakhova) note, however, [27] that when neutral or acid sodium sulfide is oxidized, no sodium disulfide is recovered, but only sodium sulfite, thiosulfate, and sulfate; 2) the action of sodium sulfide or hydrosulfide upon cellulose dixanthide, as in our experiment; 3) the reaction of sodium sulfide with free sulfur, which may enter the viscose together with the carbon disulfide, etc. The sodium sulfide may possibly split off sulfur from the perthiocarbonate.

In the presence of free carbon disulfide no appreciable quantities of the sodium disulfide can exist in the viscose, since it would then react with the carbon disulfide to form sodium perthiocarbonate.

Various data, though of an indirect sort, justify the assumption the viscose contains sodium disulfide; there can be no doubt any longer that sodium sulfide exists in viscose. We still have to find a direct method of discovering the

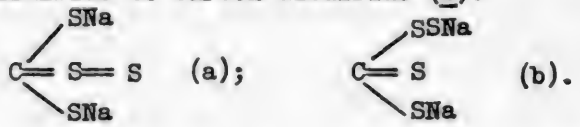
disulfide in viscose, though the method of cadmium precipitates and treatment with sulfur-removing substances indicates the presence of the disulfide and the perthiocarbonate.

The synthetic preparation of sodium disulfide offers no difficulties (best of all is the action of carbon disulfide upon alcoholates, followed by the addition of sulfur in a current of anhydrous hydrogen). It is difficult to prevent its oxidation to the thiosulfate; no air must be allowed to enter the apparatus. The recovery of sodium disulfide from viscose is difficult. A direct method of isolating the disulfide from viscose is still to be developed.

Trithiocarbonate and perthiocarbonate. These substances are conveniently synthesized by existing methods, but they are usually contaminated by some impurities and they are stabler in the form of hydrates with varying percentages of water. Syntheses of these substances have been described in the papers by Ueoman [9] and by Halban and associates [28].

The first definite information on the trithiocarbonate was obtained in the first half of the last century; Gelis was the first to synthesize and isolate the perthiocarbonate (1875).

After the work done by Berzelius it was thought that polysulfides react with carbon disulfide to liberate sulfur, yielding compounds with the formula $CS_2 \cdot MS_4$. Gelis showed [29] that in reality, when a disulfide, a trisulfide, or a tetrasulfide of a metal reacted with carbon disulfide, the only compound formed is $CS_2 \cdot MS_2$, a large amount of heat being evolved, as more precisely set forth in Ueoman's paper. Gelis notes that sulfur causes the trithiocarbonate to convert into sulfocarbonates of the disulfides. He proposed the use of sulfocarbonates of metallic disulfides to isolate metallic polysulfides from the sulfocarbonates, employing the insolubility of the former in alcohol (in contradistinction to sodium perthiocarbonate). The problem of the structure of the perthiocarbonates is still unsolved. Most often they are given a formula with quadrivalent sulfur (a), although a different formula, making the perthiocarbonate formula resemble that of the thiosulfate, is not without a certain plausibility, namely, as the result of adding sodium disulfide to carbon disulfide (b):



The perthiocarbonates should not be confused with the orthothiocarboxylic acids, known as their alkylated derivatives $C(SR)_4$ [30], but not as salts (tetrathiocarbonates).

As Ueoman has pointed out, the perthiocarbonate is converted into the trithiocarbonate by potassium cyanide. Conversely, adding an atom of sulfur to the trithiocarbonate converts it into the perthiocarbonate.

We added flowers of sulfur to the trithiocarbonate; in the course of a week it dissolved completely and was added chemically to the trithiocarbonate, the color of the solution changing from red (or pink) to a yellow-orange. Diluting the solution caused its color to change to a pure yellow. The trithiocarbonate and the perthiocarbonate were obtained as crystalline salts. The composition of the crystals of trithiocarbonate agreed fairly accurately with the formula $Na_2CS_3 \cdot 3H_2O$. They are small yellow-orange needles that dissolve as a red solution. The trithiocarbonate prepared by Ueoman's method is free from the perthiocarbonate, as is indicated by the absence of a reaction with potassium cyanide.

A few experiments were tried to react the perthiocarbonate with alkyl halides to obtain typical derivatives, but no such derivatives were secured. For example, when the perthiocarbonate was reacted with benzyl chloride, ethyl bromide, chloroacetic acid ester, and the like, substances were obtained with a sulfur content below that required for the perthiocarbonate.

The trithiocarbonate and the perthiocarbonate react with p-nitrophenyldiazonium; with the trithiocarbonate the precipitate is brown, whereas with the perthiocarbonate it is orange. But these substances, which are soluble in benzene, cannot be recrystallized without decomposing. The analysis for sulfur yields figures that are close to the theoretical content, although the errors are appreciable.

The properties of the trithiocarbonate and the perthiocarbonate as found by us agree with those set forth by Ueoman and Halban, including the absorption spectra of the visible spectrum. The crystals contain varying percentages of water of hydration.

In the analysis of the precipitate with cadmium salts for carbon disulfide and hydrogen sulfide after acid treatment (Danilov and Rizov), free sulfur was found in the residue; it was determined quantitatively by the hypobromite method and indicated the percentages of sulfur-yielding (perthiocarbonate and disulfide). After removal of the precipitate the filtrate was analyzed in the usual manner for sulfite and hyposulfite. If sodium sulfite is put into the viscose to begin with, no free sulfur is found in the cadmium precipitate, and the thiosulfate accumulates.

We were unable to determine the perthiocarbonate potentiometrically with a silver electrode, whereas a stage is obtained for the trithiocarbonate at 600-500 millivolts, and for sodium sulfide at 800-650 millivolts.

Sodium sulfite and thiosulfate. These two salts were found in small quantities in viscose a long time ago. In particular, the quantity of the thiosulfate in viscose increases when sodium sulfite is added to the viscose or to the alkali cellulose before xanthation. The two salts are found in the filtrate after the sulfur compounds and the thiocarbonates have been precipitated as cadmium salts. The percentage of each of these salts is determined quantitatively by titrating their mixture with iodine, then determining the sulfite by the formaldehyde method as a strontium salt, and again titrating the remaining thiosulfate with iodine. The accumulation of thiosulfate when sodium sulfite is added to viscose indicates that the viscose contains other substances besides the thiosulfate that can give up an atom of sulfur to potassium cyanide.

The presence of sulfite and thiosulfate in viscose has been noted, for instance, in the paper by Tanemura and Miyoshi [13].

The amount of sodium sulfite that disappears after this salt is added to the viscose ranges from 10 to 30% (the first 10% disappears very fast); the thiosulfate is found to increase, with an excess of the compensating sulfite ion, which indicates the existence of other causes for the formation of thiosulfate. The sodium sulfite in viscose may be formed by the hydrolytic and oxidative transformation of the trithiocarbonate and the oxidation of the sodium sulfide.

The sodium thiosulfate is formed: 1) as a result of the oxidation of sodium disulfide, sodium perthiocarbonate, and sodium trithiocarbonate; 2) as a result of the addition to the sulfite of free sulfur or of sulfur detached from other sulfur-containing compounds; and 3) by the action of sodium sulfide and sodium sulfite upon the dixanthides.

2. Ratio of Viscose Components to Sulfur-Detaching Substances

The ability of low-sulfur substances to add free sulfur or to detach it from other substances containing several sulfur atoms is well known.

a) Action of sodium sulfide upon a dixanthide. Sodium sulfide readily adds free sulfur, changing into sodium disulfide. It is known that organic tri- and tetrasulfides (orange in color), with a formula $S_x\left(C(=S)OC_2H_5\right)_2$ where X=1 to 4, are converted into disulfides when acted upon by sodium sulfide [31]. All the organic sulfides are reduced to mercaptides by heating with an alcoholic solution of potassium sulfide, potassium disulfide being formed; when an alkali is present, a thiosulfate is formed [32]. For the celluloses, however, only the dixanthides of the sulfide group (Cross and Bevan, 1893) [15] and the thioanhydrides (Danilov, Brokhina, and Grad, 1934, 1947) [33,34] are known. No sulfides with a large number of sulfur atoms are known for the celluloses. Nor is there any description of a conversion of dixanthides of alcohols to thioanhydrides when reacted with sodium sulfide. We explored the action of sodium sulfide upon cellulose dixanthide. Our data likewise indicate that the action of sodium sulfide upon the dixanthide does not yield a thioanhydride of cellulose xanthic acid, though polysulfide substances do accumulate. Even Kolbe's textbook [35] describes the action of sodium sulfide and sodium hydrosulfide upon diethyl dixanthide. With the former the dixanthide is cleaved, forming two moles of xanthate and free sulfur. With the latter, the action of sodium hydrosulfide, NaHS, also yields two molecules of the xanthate, in addition to hydrogen sulfide and free sulfur. The production of free sulfur indicates the possible formation of the disulfide thereby.

We (Danilov and Grad) explored the action of sodium sulfide upon cellulose dixanthide. The dixanthides we used in our experiments had 13.4% of sulfur and 76.07% of cellulose. To a colorless suspension of the dixanthide in water we added a colorless solution of pure sodium sulfide, in an amount slightly exceeding the equivalent quantity, based on the reaction of one molecule of sodium sulfide with ¼ of the sulfur in the dixanthide, which corresponds to the formation of the thioanhydride. After 2 to 4 hours had elapsed, the solution acquired an intense yellow color. The color of the cellulose derivative changed from white to greenish (the usual color of cellulose xanthate), and the next morning gelatination had set in, owing to the ripening of the xanthate formed. No free sulfur was detected. The formation of a xanthate was confirmed by the fact that after the precipitate had been filtered out, repeatedly washed with alcohol, and dissolved in water (it doesn't all dissolve), and after it had been acidulated with acetic acid and treated with iodine, the white precipitate of the dixanthide was reconstituted. Further proof of the fact that sodium sulfide cleaves a dixanthide into a cellulose xanthate is the fact that the reaction products yield characteristic precipitates with salts of the heavy metals (zinc and copper). The filtrate recovered after the coagulated xanthide has been filtered out contains, in addition to sodium sulfide, polysulfurized products (but apparently no free sulfur), as is shown by the formation of potassium thiocyanate when potassium cyanide is added to the filtrate. The potassium thiocyanate is determined by means of the usual reactions. It is noteworthy that adding potassium cyanide changes the color of the filtrate to pale yellow instead of an intense yellow, but not to pink (the latter is characteristic of viscose, owing to the accumulation of the trithiocarbonate). Tests for the presence of the trithiocarbonate were negative. It may be assumed that the formation of potassium thiocyanate is due to the presence of (yellow) sodium disulfide in the filtrate, and not to the thiosulfate, which yields up its sulfur to potassium cyanide with

difficulty and is not colored. The initial filtrate produced by the action of sodium sulfide upon the dixanthide was treated with cadmium carbonate to precipitate sodium sulfide and disulfide. This filtrate reacts with iodine solution. Treatment with strontium carbonate did not yield a precipitate, even after the lapse of 24 hours, which indicates that no sodium sulfite is present. Reactions with silver nitrate and with acids enable us to conclude that the solution contains sodium thiosulfate. Repeated tests with other samples of cellulose dixanthides showed that the action of sodium sulfide upon cellulose dixanthide gives rise to cellulose xanthate, which quickly coagulates, with a yellow supernatant solution containing sodium disulfide and sodium thiosulfate.

b) Action of sodium sulfite upon dixanthides. Sodium sulfite is converted into sodium thiosulfate by the addition of sulfur. An alkali sulfide is formed when sodium sulfite acts upon an alkali polysulfide; the sulfite turning into a thiosulfate in the presence of free sulfur; and organic disulfides can give up one of their sulfur atoms to sodium sulfite.

The action of sodium sulfite upon dixanthides was explored in our experiments. We shall describe an experiment (by Danilov and Grad) with diethyldixanthide (m.p. 32°).

A solution of 1.2 g of sodium sulfite in 15 ml of water was added to 2.0 g of diethyldixanthide dissolved in 60 ml of alcohol. The precipitate of mineral salts was filtered out after 30 minutes had passed, 0.4 g of unreacted diethyldixanthide settling out after the filtrate was diluted with water. The alcohol was driven off from the mother liquor; the resultant aqueous solution was colored slightly greenish. The solution produced no precipitate with cadmium salts, which indicates the presence of hydrogen-sulfide derivative. The sulfite was precipitated as the strontium salt; the presence of sodium thiosulfate in the resulting filtrate was proven by its characteristic reaction with silver nitrate and by the recovery of sulfur by acidulating the heating the test solution. In two other experiments, the time of the reaction of diethyldixanthide with sodium sulfite was increased from 2 to 6 hours, efforts being made to recover substances without diluting them with water. No thioanhydride was found in any experiment. One experiment was run with diethyldixanthide and sodium bisulfite in a water-alcohol medium. Nor in this case was thioanhydride recovered, though the presence of sodium thiosulfate was proved. Thus, sodium sulfite detaches a sulfur atom from the dixanthide, but we have been unable to prove the formation of the thioanhydride.

c) Action of potassium cyanide (sodium) as a method of determining polysulfide substances in viscose. As a reagent for polysulfurized compounds, potassium cyanide is able to detach one of the sulfur atoms in the molecule, which has been under investigation in our laboratory during various years.

We (S. N. Danilov) have expressed the hypothesis that viscose contains polysulfurized products: disulfides and perthiocarbonates (with the exception of thiosulfate), that can deliver sulfur to potassium cyanide, sodium sulfite, and sodium arsenite. Danilov and Rizov have pointed out the similarity in the action of potassium cyanide, sodium sulfite, and (later) sodium arsenite and sometimes even polythionates upon viscose, consisting of the ability of these substances to detach sulfur from polysulfide products. The turning pink of viscose when sodium sulfite or sodium arsenite is added to it, and especially when sodium (potassium) cyanide is added, was explained [24] as the result of detaching sulfur from the yellow perthiocarbonate solution, converting it into the orange trithiocarbonate solution, and of converting the yellow disulfide solution to the colorless sodium sulfide solution. The paper by Danilov and Grad [34] showed that cellulose dixanthide likewise loses an atom of sulfur in the presence of cyanides, the white

dixanthide being turned into the greenish xanthate. We found that the pink color of the trithiocarbonate solution takes on a noticeable orange-yellow tint when as little as 2-3% of the perthio salt is added. The introduction of potassium cyanide quickly restores the original pink color. Large amounts of the perthiocarbonate are not needed to produce the corresponding color reactions. The greenish hue of the xanthate may be admixed with the color produced by these conversions from the perthiocarbonate to the trithiocarbonate, and vice versa.

In our research we explored the detaching of sulfur from various compounds in viscose by the cyanide method.

Tests in our laboratory indicated that when a 15% solution of caustic soda with an excess of carbon disulfide is added to a solution of the trithiocarbonate (not entirely pure), produced by standing for three days without exposure to air, and the mixture is then heated to 50° for 3 hours to eliminate the excess carbon disulfide, thus adding a definite amount of sulfur as calculated by iodometric determination, the sulfur dissolved completely after 2 to 3 weeks, and the solution turned from red to dark orange, as has been pointed out by Ueoman as well [8]. When the solution was diluted, the color was found to be pure yellow, whereas the initial trithiocarbonate solution remained pink in the absence of air for as much as three weeks until the sulfur was added, acquiring a slight orange tint that vanished when potassium cyanide was added, however.

We repeatedly synthesized pure preparations of the tri-and perthiocarbonate in crystalline form (by Ueoman's method). The sodium disulfide was produced by absorbing hydrogen sulfide in alcohol and dissolving sulfur in the sodium hydrosulfide formed; this ensured our getting a preparation that was freest of any traces of the thiosulfate. In its crystalline form the trithiocarbonate consists of brown crystals that produce a pink or red solution. When potassium cyanide is added to a solution of the trithiocarbonate prepared by the Ueoman method, no potassium thiocyanate is formed, i.e., it is free of the disulfide, the perthiocarbonate, and the thiosulfate.

In its crystalline form the perthiocarbonate is a yellow-orange substance that forms yellow solutions. The addition of potassium cyanide or sodium sulfite to solutions of the perthiocarbonate causes the color to change from yellow to pink. The colors produced by these conversions from the perthiocarbonate to the trithiocarbonate and from sodium disulfide to sodium sulfide change the usual color of the viscose to a pinkish one. Adding twice the theoretically required amount of potassium cyanide promotes the quantitative conversion of the perthiocarbonate into the trithiocarbonate. Here, as in other instances, the potassium thiocyanate that formed was determined by the customary methods, with some modifications in the analytical procedure that proved desirable in each individual case. With mixtures of the perthiocarbonate and the trithiocarbonate, the trithiocarbonate could be decomposed with dilute acid, the carbon disulfide and the hydrogen sulfide removed by scavenging, and (after neutralization) the thiocyanate determined argentometrically, adding dilute nitric acid in the presence of the cyanide. It is better, however, to convert the trithiocarbonate, like all derivatives of carbon disulfide and thiocarbonic acids, into cadmium salt derivatives, and to analyze the filtrate argentometrically for potassium cyanide and thiocyanate, using Liebig's and Volhard's methods and allowing for possible traces of sodium thiosulfate and sulfite; the latter are determined iodometrically by the usual methods (via the strontium salt or by the formaldehyde method). The quantity of potassium thiocyanate corresponded exactly to the amount of the perthiocarbonate used (Danilov and Borobyeva). In a separate test it was proved that when a mixture of the perthiocarbonate and the trithiocarbonate purposely made up with potassium cyanide was titrated against lunar caustic after it had been acidulated in the cold

with nitric acid, it yielded exactly the same quantity of the thiocyanate, and hence of the perthiocarbonate, even when the latter constituted no more than 5% of the mixture with the trithiocarbonate. In these tests the aggregate concentration of the tri- and perthiocarbonate together was 2%. Correspondingly, twice the amount of potassium cyanide calculated to be required for the perthiocarbonate in the mixture was added. Experiment showed that perthiocarbonate purposely introduced into viscose can be determined by means of potassium cyanide.

A control experiment showed that the thiosulfate yields up its sulfur to cyanide much more slowly than the perthiocarbonate, but even in this instance the thiosulfate was finally converted into sodium sulfite (requiring 4 days with a 2% concentration of sodium thiosulfate and twice the excess of cyanide over the quantity required by theory). At first, the sulfur atoms are detached more rapidly, but the reaction later slows down: during the first 24 hours approximately 40% of the thiosulfate is converted into the sulfite; 30% is converted during the next 24 hours; 20% during the third day; and approximately 10% during the fourth and last day. Here, too, the quantity of the thiocyanogen ion formed is exactly equivalent to that of the sulfite ion produced.

In exactly the same way, the yellow solution of the disulfide is rapidly bleached when potassium cyanide is added, forming sodium sulfide and thiocyanate, which was also specially checked in our experiments.

Pure sodium disulfide, prepared from an alcoholic solution of sodium sulfide nonahydrate and the stoichiometrical quantity of sulfur by heating to 30° over a water bath, crystallized as yellow needles ($Na_2S_2 \cdot 5H_2O$) after the brown solution (83.3 g of $Na_2S \cdot 9H_2O$, 200 ml of alcohol, and 11 g of sulfur) had cooled. A special test showed that adding 3% of caustic soda to the disulfide solution (0.3% concentration of Na_2S_2) does not bring about the conversion of the sodium disulfide into the thiosulfate (precipitating the sodium sulfide with cadmium carbonate and separating the thiosulfate from the sulfite by Kurtenacker's method). The solution retains its yellow color for a long time in the presence of alkali. The readiness of the disulfide to react with carbon disulfide, which is usually present in viscose during various stages of the latter's manufacture and ripening, indicates that much of the disulfide in the viscose must be transformed into the perthiocarbonate.

We elaborated several variants of the quantitative computation of the viscose substances that can yield up their sulfur atom to potassium cyanide, principally for detecting the perthiocarbonate.

The quantitative determination of sodium perthiocarbonate in viscose as it ripens was done by determing the quantity of potassium thiocyanate present after the cyanide had been added. It should be kept in mind, however, that cyanogen salts can retard the chemical and colloido-chemical ripening of the viscose, if they are added a few days before the analysis for the thiocyanate. That is why, in the investigation of the accumulation of sulfur-yielding substances, it is advisable to add the potassium cyanide to the viscose samples on various ripening days instead of all at once likewise bearing in mind that potassium cyanide may itself partly change the amount of the perthiocarbonate ion as compared to viscose containing no cyanide. Allowance can be made for the thiocyanate formed from the thiosulfate by the amount of the sodium sulfite formed. It is harder to ascertain the consumption of cyanide for the disulfide and the perthiocarbonate so that these two substances are allowed for summarily.

The amount of thiocyanate formed in the viscose can be determined by

precipitating the xanthate and the sulfur compounds with lead acetate and as cadmium salts. When the sulfur compounds are precipitated with lead acetate, care must be taken to avoid an excess of the precipitating agent, since lead thiocyanate often appears in the precipitate when an excess of lead acetate is used, even though it is soluble when the solution contains 2.5-3% of free caustic soda. An adequate quantity of alkali must be present to prevent the precipitation of lead sulfate and sulfite.

We developed the following procedure. With a viscose containing about 7% cellulose and an aggregate alkalinity of 7%, approximately 1 ml of a saturated solution of lead acetate must be used per gram of viscose to produce transparent filtrates containing the cyanogen ion. Potassium cyanide is added at various stages of the viscose's ripening or else all the potassium cyanide is added at the commencement of ripening in order to determine the substances in the viscose that can transfer an atom of sulfur to the cyanide. Silver nitrate is used to determine the resulting cyanide in the filtrate as silver thiocyanate, after the xanthate and the carbon disulfide derivatives have been precipitated with lead acetate. The percentage of thiocyanate found must be corrected, however, if the solution contained appreciable amounts of sodium chloride, which is titrated back together with the cyanide and the thiocyanate in a nitric-acid medium. The amount of thiocyanate is determined quantitatively by separately measuring the potassium cyanide and the sodium chloride in the viscose (cf. Treadwell, Volumetric Analysis). We may state, in passing, that the viscose becomes a transparent reddish-orange a few hours after the potassium cyanide has been added; its previous dark color disappears because the iron salts enter solution as coordination compounds. If a sulfite is added to the viscose instead of the potassium cyanide, the viscose turns reddish, but its color remains dark, and it does not become full transparent.

It was proved experimentally that 100% of the added potassium cyanide (20% by weight of the alpha cellulose in young viscose) is found unchanged in the viscose immediately after it had been added without any of it having been changed into the thiocyanate. But when we take viscose that has been ripened for an increasingly long period and subject it to analysis for polysulfurized products, introducing potassium cyanide into it is accompanied by the formation of thiocyanate. Table 1 gives the growth of sulfur-yielding substances in viscose as the latter ripens, in per cent of the thiocyanate formed.

TABLE 1

Growth in the Amount of Potassium Thiocyanate in Viscose in Per Cent of Sulfur

Days of Ripening	1	2	4	5	8	10
Per cent of cyanogen sulfur.....	0.02	0.06	0.12	0.14	0.21	0.22

Thus, the products that can yield up an atom of sulfur accumulate in viscose only with the passage of time. If we assume that all the detached sulfur comes from sodium perthiocarbonate or sodium disulfide, it must be said that no

more than 0.22 X 4 = 0.88% of perthiocarbonate and disulfide sulfur accumulates in viscose after 12 days of ripening. Separate allowance must be made for the percentage of thiosulfate in the viscose. Precipitation by lead salts is useless, as lead salts of sulfuric and sulfurous acids may be precipitated.

Other methods had to be employed, cadmium salts, and later on, salts of cobalt. We initially did our research with cadmium salts, which made it possible to get a filtrate containing the sulfite, thiosulfate, thiocyanate, and cyanide, although sulfite and thiosulfate may be found in the precipitate as well. The cadmium salt method, ordinarily recommended in analytical chemistry for determining sulfur compounds, is employed in analyzing viscose for its sulfates and thiosulfates. Sometimes a saturated solution of sodium chloride is added to the viscose to obtain transparent solutions (R. S. Neiman [6]); this does not always guarantee the preparation of transparent solutions, however (some of the sulfurized cadmium separates out as a cloudy suspension), and it is quite inadvisable whenever an analysis has to be made for thiocyanates, as in the present instance (the excess of silver chloride interferes). When soluble cadmium salts are used and the filtrate is neutral, no colloidal suspensions are observed, but then more cadmium salts are required than when cadmium carbonate is used. We used the cadmium method in our experiments to compute the sulfur-yielding substances and to ascertain the accumulation of sulfites and thiosulfates in ordinary viscose (without additives). Whenever necessary, the cadmium precipitates were analyzed by the method adopted in our laboratory (Danilov and Rizov [7]). We employed cadmium carbonate, freshly precipitated from a saturated solution of cadmium nitrate by a concentrated solution of soda, without washing out the saltpeter that forms, as it is required for good filterability. When we add 5 ml of a suspension of cadmium carbonate not freed from saltpeter to 1 g of viscose, we get completely transparent filtrates. Analysis is continued in a carbonic-acid medium for the sulfite and thiosulfate ions (Kurtenacker method) and for the thiocyanogen ion with a silver reagent after the solution has been acidulated with nitric acid.

We investigated various viscoses with identical percentages of cellulose and alkali, both with and without additions of sodium sulfite (cf. Fig. 1 and Table 2) and of the latter mixed with potassium cyanide. Analyses were made immediately after the sodium sulfite had been added to the viscose. Viscose without any additive required 0.16 ml of an 0.1N iodine solution for the thiosulfate in 1 g of cellulose; i.e., the thiosulfate sulfur totaled 0.1%. The same percentage of the S_2O_3 ion was found in "sulfite" viscose immediately after the additive had been introduced, whereas the percentage of sulfite found corresponded to the percentage of sulfite added. In subsequent analyses, the percentage of sulfite found diminished after the passage of various intervals of time, being expressed in percentages of the amount introduced initially. Comparison of the rise in the percentage of the thiosulfate with the loss of sulfite indicated that the drop in sodium sulfate was compensated by the increase in newly formed thiosulfate, since the sum total of both salts remained the same. There is very little of its own sulfite in the viscose, there being more of the thiosulfate, and part of the sulfite may be converted into the thiosulfate. This indicates that the origin of the thiosulfate is not only the detaching of sulfur from sulfur-yielding substances by the sulfite, but other sources as well, in particular, oxidation of the sodium sulfide, disulfide, trithiocarbonate, and perthiocarbonate. But the viscose was in a closed container; this means that only previously absorbed oxygen and some other reactions can have affected the viscose.

When we compared the percentage of cyanogen sulfur with that of the thio-

sulfate sulfur in the viscose without additives at the end of the experiment, we found that if all the thiosulfate that formed had given up its sulfur (one atom of sulfur per molecule of cyanide), only 0.13% of cyanogen sulfur would have been formed, whereas 0.22% had actually been formed. The percentage of cyanogen sulfur formed exceeds that of the sulfite sulfur formed at the same time. The percentage of thiosulfate in the "cyanide" viscose is lower than in the ordinary viscose, as part of it was converted into sodium sulfite and thiocyanate was formed.

The thiosulfate cannot be the sole source of the thiocyanate formed. The percentage of thiosulfate in normal viscose rose to 0.4% of thiosulfate sulfur during the course of 4 weeks, as is confirmed by Table 3 (Fig. 2) for another series of tests. During this same period, two-thirds of the added sulfite was converted, chiefly into the thiosulfate (20% of $Na_2S_2O_3$ was added to the alpha cellulose, and an equivalent quantity of potassium cyanide was added to the "cyanide" viscose). The percentages of both the thiocyanate sulfur and the sulfite sulfur increased in the cyanide viscose, but the percentage of thiocyanate sulfur is always higher than that of the sulfite formed.

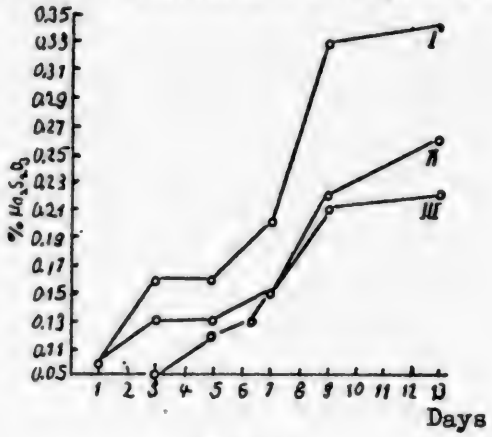


Fig. 1

I—Sulfite viscose; II—ordinary viscose; III—per cent of KCNS (viscose + KCN).

At first, the percentage of thiosulfate in the "cyanide" viscose rises (apparently, the thiocyanate is formed from the compounds that yield up sulfur more easily than the thiosulfate); then it passes through a maximum and begins to fall, as the conversion to sodium sulfite begins to make its appearance.

The "total sulfur" of the three components (perthiocarbonate, disulfide, and thiosulfate) in viscose with potassium cyanide added ends up as a constant figure, since all that happens is a redistribution of the sulfur, with potassium thiocyanate being formed, and especially with the sulfite being accumulated at the expense of the sodium thiosulfate. The percentage of sulfite in cyanide viscose at the end of the ripening period was found to correspond to the total of the thiosulfate formed in "normal viscose" (0.19 and 0.40). The thiocyanate is, apparently, most easily formed from the perthiocarbonate, followed by sodium disulfide. There is not much reason to assume the presence in the viscose of polythionates or even of the trithionate, which is more stable in an alkaline medium and, like sodium sulfite, possesses some ability to add an atom of sulfur. In these tests we did not take into account the possible formation of a dixanthide, though a small amount ought to accumulate owing to the alkalinity of the viscose.

When determining the thiocyanate in the presence of excess sodium (or potassium) cyanide, it is advisable to eliminate the hydrogen cyanide evolved during acidulation with nitric acid. Heating may cause a change in the thiocyanic acid, however. It is best to remove the hydrogen cyanide with carbonic acid.

TABLE 2

Transformations in Viscose to Which Sodium Sulfite and Potassium Cyanide Have Been Added

Research object	Component	Days elapsed						
		1	3	5	6	7	9	13
Viscose without additive	Thiosulfate, %	0.1	0.13	0.13	—	0.15	0.22	0.26
Viscose with sulfite added	Thiosulfate, %	0.1	0.16	0.16	—	0.20	0.32	0.33
	Sulfite (in per cent of initial value)	100	93	93	—	80	73.8	52.5
Viscose with potassium cyanide added	Thiosulfate S, %	—	—	—	—	—	—	0.18
	Sulfite S, %	—	—	—	—	—	—	0.03
	Cyanogen S, %	0.02	0.06	0.12	0.13	—	0.21	0.22

TABLE 3

Research object	Component	Days elapsed								
		1	3	7	12	16	20	25	28	30
Viscose without additive	Thiosulfate S,%	0.11	0.13	—	0.19	0.22	0.29	0.39	0.4	Coagulation
Sulfite Viscose	Thiosulfate S,%	0.10	0.17	—	0.29	0.30	0.35	0.50	—	0.81
	Sulfite S in per cent of initial amount	100	87.7	69.5	—	60	59	37.6	—	36.4
Cyanide viscose	Thiosulfate S,%	0.11	0.14	0.21	0.21	0.26	0.20	0.15	0.09	Coagulation
	Sulfite S,%	—	0.03	0.03	0.09	0.12	0.15	0.19	—	—
	Thiocyanogen S,%		0.13	0.14	0.18	0.20	0.22	0.25	—	—
	Total S,%	0.11	0.30	0.38	0.53	0.52	0.52	0.53	—	—

The method of analysis of mixtures of the substances in viscose that contain sulfur boils down to this: first of all, with the CS_3", S", CN', CNS', SO_3", and S_2O_3" ions present, the derivatives of carbon disulfide and thiocarbonic acids are precipitated; CN', CNS', SO_3", and S_2O_3" remain in solution. The alkaline solution is neutralized against phenolphthalein, sodium bicarbonate is added, and carbon dioxide is passed through the heated solution, all the prussic acid being eliminated (criterion: the outgoing gas produces no suspension in a silver nitrate solution). Incomplete elimination of the prussic acid causes errors in titrating with silver and in the iodometric determination of sulfite and thiosulfate, since hydrogen cyanide differs from thiocyanic acid in that it reacts with iodine in an acid solution. The thiocycanate is determined by titration with silver nitrate in a nitric acid medium. In the presence of an excess of carbon dioxide the sodium thiosulfate may be titrated back incorrectly. Since the SO_3" ion can be separately determined by precipitation as strontium salts, the thiosulfate can be

ascertained by computation from the overall titration with iodine. The sulfite can be determined by means of formaldehyde, and the thiosulfate by iodometric titration (Kurtenacker).

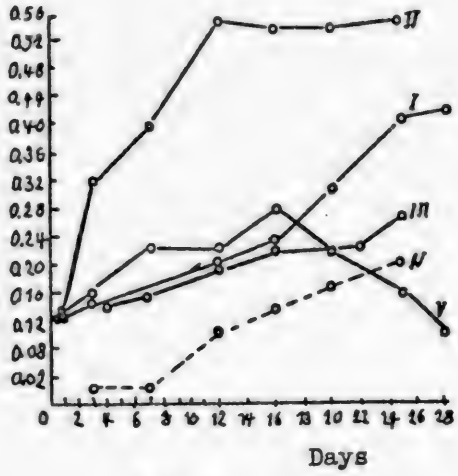


Fig. 2

I—Per cent of $Na_2S_2O_3$ (viscose without additive); II—Per cent of total sulfur (viscose + KCN); III—per cent of KCNS (viscose + KCN); IV—per cent of $Na_2S_2O_3$ (viscose + KCN); V—per cent of $Na_2S_2O_3$ (viscose + KCN).

Besides determining the "thiocyanate" sulfur, we also have to know the percentages of sodium trithiocarbonate (and perthiocarbonate) and sulfide and (disulfide) in viscose.

The important components in viscose can be determined by making an analysis of the cadmium precipitates for hydrogen sulfide and carbon disulfide (Danilov and Rizov [24]), making a Bernhardt analysis (for trithiocarbonate and sulfide), and determining the sodium sulfide potentiometrically (Neiman and Kargin).

Whether sodium sulfide is present in the viscose, and its percentages if present, can be ascertained by: titration with a silver electrode, the initial compensation voltage, and the curve of the latter's drop. (The known sodium sulfide added to the viscose is titrated back, however, with a large excess—as much as 20-25% at times. Hence, the figures obtained cannot be taken as absolute values.). The sulfide area is found to be 800-650 millivolts, and the trithiocarbonate area 600-500 millivolts, which agrees with the figures given by Neiman, Kargin, and Fokina [18]. The percentage of sodium sulfide is as high as 0.25% in young viscoses, whereas the percentage in overripe viscoses is extremely small, barely perceptible. The perthiocarbonate cannot be determined potentiometrically in viscose. Pure perthiocarbonate is titrated back at the same millivoltages as the trithiocarbonate. In mixtures, the trithiocarbonate and the perthiocarbonate are titrated together, and no potential discontinuity can be detected. The ease with which the trithiocarbonate is hydrolyzed and oxidized is a great handicap.

To determine the growth of sodium sulfide, Na_2S, and trithiocarbonate, NA_2CS_3, in viscose in the presence of potassium cyanide, we measured the percentage of sodium sulfide in viscose potentiometrically, with the cyanide present and absent. The figures are given in Table 4.

The percentage of sodium sulfide in viscose obviously increases when cyanide is present, either because it is partially formed from the disulfide or because its conversion at the expense of the free carbon disulfide or the dithiocarbonate groups in the trithiocarbonate is inhibited. When sodium sulfide is introduced into the viscose, it is found to vanish within a few days, evidently because of its conversion into the trithiocarbonate. It is worthy of note that if sodium sulfite is introduced into the viscose together with the sodium sulfide, it is only after some time (several days) has elapsed that the percentage of sodium sulfide drops appreciably, and when this is so, the percentage of sodium sulfide rises sharply when potassium cyanide is added.

TABLE 4

Research object	Results of determinations	Days elapsed			
		1	4	7	11
Normal viscose	a) Ripeness according to NaCl	6.4	2.0	0.3	0.0
	b) Na_2S (%)	0.27	0.19	0.14	0.08
	c) Na_2CS_3 (%)	0.77	1.12	1.57	1.89
	d) Thiosulfate S, %	0.09	0.16	0.17	0.22
Viscose with potassium cyanide added	a) Na_2S (%)	—	0.53	0.57	0.90
	b) NA_2CS_3 (%)	—	1.38	1.38	—
	c) Thiosulfate S, %	0.1	0.15	0.20	0.21
	d) Sulfite S, %	—	0.02	0.02	0.01
	e) Thiocyanate, %	—	0.05	0.10	0.13

TABLE 5

Changes in the Percentages of Na_2S and Na_2CS_3 in viscose, With and Without Additives (0.38% by weight of the viscose of Na_2S and Na_2SO_3)

Research object	Ripeness	Per cent	
		Na_2S	Na_2CS_3
Normal viscose without additives.	8	—	—
Viscose with Na_2S.	0	0.11	3.85
Viscose with $Na_2S + Na_2SO_3$	0.6	0.97	0.86

The changes in the percentages of sodium sulfide and trithiocarbonate were followed potentiometrically in two parallel experiments on viscose samples, to one of which 0.38% by weight of sodium sulfide had been added, and to the other the same percentage of sodium sulfite with an equivalent quantity of the sulfide (Table 5).

The ease with which the trithiocarbonate is hydrolyzed, forming sodium sulfide and the latter's oxidation products, as well as the ease with which the trithiocarbonate is oxidized must be borne in mind. It was found advisable to add a small amount of sodium sulfite (0.3% in solution) in the potentiometric titration of the trithiocarbonate with a silver electrode in order to eliminate oxidation of the trithiocarbonate.

When titrating mixtures of Na_2S and Na_2CS_3 that contain no free caustic soda, one must add caustic soda (2-2.5% in solution) to prevent the Na_2S from hydrolyzing to the hydrosulfide. When no alkali is present, there is no potential discontinuity during the transition from the sulfide (Na_2S) to the trithiocarbonate (Na_2CS_3); when free alkali is present, however, a discontinuity appears at a certain voltage, after which titration of the trithiocarbonate begins.

3. Reaction of Sulfur-Detaching Substances with Sodium Disulfide

(Experiments by S. N. Danilov and A. F. Vorobyeva)

As there is no doubt about the presence of sodium disulfide in viscose, we were very much interested in studying the reactions of this substance with sulfur-detaching substances. Pure sodium disulfide was prepared for this research.

Dry carbon disulfide (dried over calcium chloride) was passed through an alcoholic solution, chilled with ice water, of freshly prepared sodium alcoholate (40 ml of anhydrous ethyl alcohol, and 2.5 g of sodium). Two variants were used: 1) Half of the alcoholate was saturated with carbon disulfide, resulting in the formation of sodium sulfide; 2) all the alcoholate was saturated with carbon disulfide, which yielded the colorless crystals of sodium hydrosulfide. Then the stoichiometrical quantity of desiccated flowers of sulfur (3.2 g per 2.3 g of sodium) was added, and the mixture was heated over a water bath while a current of dry hydrogen, from which all traces of oxygen had been removed, was passed through the mixture. In both cases, the yellow crystals of the disulfide settled out when the mixture was cooled; they were quickly filtered out and dried over solid caustic potash in a vacuum to protect them against oxygen and carbon dioxide.

Sodium disulfide pentahydrate ($Na_2S_2 \cdot 5H_2O$) was prepared by dissolving 83.5 g of sodium sulfide hydrate ($Na_2S \cdot 9H_2O$) in 200 ml of alcohol heated over a water bath; the stoichiometrical quantity of flowers of sulfur (11.1 g) was then added to the solution. After the mixture had been boiled over a water bath with a reflux condenser for 30-40 minutes and then cooled, yellow crystals of $Na_2S_2 \cdot 5H_2O$ settled out; they were filtered out and kept in a vacuum exsiccator. It was extremely difficult, however, to secure a disulfide that was absolutely free of thiosulfate. Most often we had preparations that contained as much as 7-15% of thiosulfate, so that a correction had to be applied to our results, especially when determining the role played by the sulfite.

The behavior of the sodium disulfide with sodium cyanide, sulfite, and arsenite was explored. After the reaction of the disulfide with the sulfur-detaching compound had gone on for a certain time, the reaction was broken off by agitating the solution with a suspension of cadmium carbonate or with a soluble cadmium salt. In the filtrate we determined either the products of the addition of sulfur to the sulfur-detaching substances (thiosulfate for the sulfite, and the thiocyanate for the cyanide) or the percentage of unreacted additive (in the case of the arsenite). We assumed that adding the cadmium salt causes no redistribution of sulfur in the system and that the disulfide that had not reacted with the additive reacts with the cadmium salt, to form cadmium disulfide or, more likely, a mixture of cadmium sulfide and sulfur. Two ways of adding the substances were tried: 1) the disulfide was first mixed with the electrolyte under test (the additive), and then the cadmium carbonate was added; 2) the cadmium salt was added to the disulfide and then the electrolyte (the additive) was added, the mixture being agitated for some time. In the latter case we might have expected that the thiocyanate and thiosulfate would be formed at the expense of the cadmium precipitate, owing to the conversion of the disulfide into the mixture $CdS + S$ or CdS_2. It was found, however, that very large quantities of the thiosulfate, the thiocyanate, and the thioarsenate were formed almost instantaneously no matter which sequence of adding the cadmium salts was employed. The question arises: to what extent is the formation of these compounds the result of the reaction of the disulfide with the electrolyte, and to what extent is it due to reactions brought about by the introduction of cadmium salts into the system? It may be assumed that the reaction of the cadmium salt with the sodium disulfide gives rise to cadmium disulfide, CdS_2, which is extremely unstable and can easily transfer an atom of sulfur to the sulfite or another additive. If this were so, the cadmium salts would be sulfur carriers. Possibly the sulfur detached from the cadmium disulfide owing to its high degree of dispersion is so reactive that it brings about the formation of the thiocyanate, the thiosulfate, etc. It was found to be difficult to establish

exactly what part of the sulfur was transferred from the disulfide to the electrolyte before the cadmium salt was added and what part of the transfer is due to this additive.

To investigate the reaction of the cyanide with the disulfide we employed a determination of the thiocyanogen ion in the presence of ammonium ferric alums.

When cyanide and disulfide solutions are poured together and immediately acidulated with an excess of hydrochloric acid, we get an unclear and instantaneously vanishing reaction of ferric thiocyanate, as the hydrogen sulfide evolved immediately reduces the ferric iron to ferrous iron. When nitric acid is added instead of hydrochloric, we get a clear thiocyanogen reaction, which testifies to the rapidity of the reaction between the cyanide and the disulfide. The quantity of thiocyanate formed is not very great, however, and a large part of it is apparently formed as the result of adding the cadmium salt. But the more or less ready transfer of sulfur in the presence of cadmium salts can also serve as an index of the ease with which sulfur is added to one electrolyte or another of the sulfite or cyanide type. We probably can visualize the action of the additives in terms of the overall figures for sulfure transfer, as the result of an initial reaction with the sodium sulfide as well as of a secondary reaction of the cadmium disulfide or of a mixture of sulfur and cadmium sulfide or of both of them together.

The time required for bleaching a disulfide solution likewise provides us with an idea of the velocities of sulfur transfer: with equivalent concentrations of electrolyte, this time is shortest for the cyanide and longest for the arsenite.

The value obtained for the thiosulfate is higher when it is precipitated with cadmium carbonate than with a soluble cadmium salt. The source of this error cannot be the precipitation of cadmium thiosulfate, since cadmium sulfate does not yield a precipitate with an 0.1N solution of the thiosulfate. We found that the thiosulfate is not appreciably adsorbed by the cadmium sulfide resulting from the sulfide when the latter is acted upon by cadmium carbonate and sulfate. The pH of the medium, which is changed by the carbonic acid, may have some effect upon the titration of the thiosulfate.

When we used cadmium carbonate to determine the percentage of the thiosulfate in sodium sulfide, $Na_2S \cdot H_2O$, we got a much larger figure than when cadmium sulfate was used. Evidently, sodium thiosulfate partially reacts with cadmium carbonate. The insolubility of the latter salt may, however, be the source of the lower results.

In an analysis of the cyanide-disulfide system by means of a precise Liebig cyanide determination, the thiosulfate interferes, since the suspension of silver cyanide dissolves in the thiosulfate, forming a coordination salt. In determining the total consumption of silver as thiocyanate and cyanide when acidulated with nitric acid, silver sulfide is thrown down after some time has elapsed, owing to the decomposition of the silver thiosulfate. Hence, each molecule of thiosulfate corresponds to the expenditure of two atoms of silver, which enables us to make a correction for the admixture of thiosulfate. The cadmium method does give precise results in determining the unreacted arsenite, however. It was found that no exchange reaction takes place between the cadmium carbonate and the arsenite, as cadmium arsenite is insoluble in water and is precipitated as soon as the arsenite is mixed with any soluble salt of cadmium. Adding a certain quantity of a titrated solution of the arsenite to the cadmium carbonate, we find all of the latter in the filtrate.

Let us examine the principal results of our experiments on the reaction between sodium disulfide and electrolytes (additives). Three sodium disulfide reactions were investigated: 1) with sodium sulfite (Tables 7 and 8); 2) with sodium cyanide (Tables 6 and 8); and 3) with sodium arsenite (Table 9).

TABLE 6

Research object	Result of Determination	Remarks
Initial concentration NaCN	0.050 (1.0N solution)	Concentration after mixing
Initial concentration Na_2S_2	0.047 (1.0N solution)	
Per cent of $Na_2S_2O_3$ admixture in Na_2S_2.	16.2	
Per cent of reacted NaCN:		
After 15 sec	94	
After 75 sec	94	Solution was bleached
Percent of reacted Na_2S_2	99.2	

TABLE 7

Research object	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Initial sulfite concentration (based on 1N solution). . .	0.05	0.038	0.05	0.05
Initial disulfide concentration (based on 1N solution). .	0.023	0.046	0.05	0.05
Per cent of thiosulfate in the disulfide	16.0	14.8	20.3	15.3
Per cent of reacted disulfide	65.8(105 minutes)	64 (105 minutes) Noticeable coloring	61.6 (5 minutes) Intense coloring	76.5 (5 minutes)
	65.9(170 minutes)	65.3(170 minutes) much weaker coloring	63.3 (15 minutes) weaker coloring	76.6 (240 minutes) solution colored
			63.3 (50 minutes) decolorized	77.7 (1170 minutes) decolorized

Overall titration was effected with a solution of silver nitrate, employing precipitation with cadmium salts. The consumption of iodine in titrating the

thiosulfate contaminating the sodium disulfide owing to the latter's ready oxidation was multiplied by two in converting the totals in terms of silver nitrate.

TABLE 8

Research object		Results of determination	
		Experiment 1	Experiment 2
Initial concentration	sodium disulfide. .	0.05	0.048
	sodium sulfite . .	0.05	0.053
	sodium cyanide . .	0.05	0.05
Per cent	$Na_2S_2O_3$ in Na_2S_2 .	9.7	15.7
	reacted Na_2S_2 with NaCN	77.5	76.5
	reacted Na_2S_2 with Na_2SO_3	4.1	58.3

Notes: 1) In Experiment 1. The disulfide is mixed with cadmium sulfate and then the cyanide or sulfite is added.

2) In Experiment 2. The disulfide is first mixed with the sulfur-detaching substance, and then the cadmium sulfate is added.

TABLE 9

Research object		Results of determination	
		Experiment 1	Experiment 2
Initial concentration	disulfide, Na_2S_2	0.05	.0.05
	arsenite, Na_3AsO_3	0.05	0.05
Per cent	$Na_2S_2O_3$ in Na_2S_2 . . .	7.3	7.3
	arsenite consumed . .	54.4	47.5
	reacted Na_2S_2 (for the arsenite)	59.6	51.9

Deducting the amount of silver nitrate required to titrate the hydrogen cyanide and the thiosulfate from the aggregate quantity, we get the amount of thiocyanate formed. In all our experiments equal volumes of cyanide and disulfide were mixed together. Much of the sulfur is transferred via the cadmium salts.

When the sulfide and disulfide are precipitated with cadmium carbonate or sulfate and the precipitate is agitated with cyanide, the filtrate exhibits the thiocyanate reaction. The quantitative check showed that most of the cyanide is converted into the thiocyanate practically instantaneously, which uses up much of the disulfide. Other comparative tests demonstrated that cyanide exhibits the greatest ability to add sulfur as compared to the other sulfur-detaching substances. The sodium cyanide was synthesized from an alcoholic solution of caustic soda.

The results of our exploration of the reaction between sodium disulfide and sodium cyanide are given in Table 6. In all the experiments we mixed equal volumes of the disulfide and the electrolyte at the given concentrations in parts of normal solutions. The concentrations were determined in the solution after mixing to eliminate errors in the concentration determinations due to oxidation. Decolorization set in during the initial hour, whereas this required 6 hours when sulfite was added.

The experiments with sodium sulfite were run at various concentrations: in Experiments 4 and 5 (Experiment 4 is listed in Table 7), the concentrations of Na_2S_2 and $Na_2S_2O_3$ were 0.05N solutions; in Experiment 1, the concentration of Na_2S_2 was almost twice that of Na_2SO_3, i.e., an excess of sodium sulfite was present. In Experiments 2 and 3, the excess of sulfite was tenfold and eightfold, respectively, and that is why the solution was bleached so rapidly.

The transfer of sulfur from the disulfide occurs rapidly, possibly via the cadmium salt, when the suspension of cadmium carbonate is poured into the reagent mixture after they had been mixed together. Though the reaction does not proceed to its conclusion for some unknown reason, the visible coloring of the disulfide disappears.

The mixture of sodium sulfite, thioulfate, sulfide, and disulfide was analyzed in the usual manner.

A comparison of the quantity of reacted sodium disulfide with that of the sulfite and cyanide in the same test is worthy of comment. It is found that the cyanide detaches more sulfur from the disulfide during a given period of time than sodium sulfite does, as is seen in Table 8. The disulfide is precipitated by cadmium sulfate, cyanide being added to the precipitate in one instance, and sulfite being added in the other (Experiment 1, Table 80, and, conversely, the disulfide is first mixed with the cyanide or the sulfide, and then the cadmium sulfate is quickly added (Experiment 2, Table 8).

Analysis showed that 29.4% of the cyanide (Liebig method) remained unreacted, 73.3% having reacted according to the quantity of NaCNS found. As these figures show, there is an error 2-3% in the analytical method. The error is due to the solvent action of the thiosulfate upon the silver cyanide, which increases the resultant figure in the Liebig cyanide determination. The Volhard method of analyzing a mixture of CN' + CNS' in the presence of S_2O_3" may be considered satisfactory.

In the case of the arsenite, we confined ourselves to a rapid pouring of the components together. In Experiment 1 (Table 9), the arsenite was added to the disulfide, with the cadmium carbonate added immediately thereafter. Three hours later we determined the unreacted arsenite in the filtrate. In Experiment 2 (Table 9), cadmium carbonate was added to the disulfide solution, and the arsenite was added 15 minutes later. The experiment demonstrated that there is no essential difference involved in changing the order in which the components are mixed together.

Control tests showed that precipitations with cadmium carbonate in a weakly alkaline medium (with a slight excess of Na_2CO_3) facilitates the maximum transfer of sulfur from the disulfide to the sulfur acceptor. When cadmium sulfate is used as a precipitant (in a slightly acid medium), the sulfur transfer is slowed down (tests with the arsenite can be performed only with cadmium carbonate, since the sulfate would precipitate cadmium arsenite, $Cd_3(AsO_3)_2$). These tests should be compared with the tests with the sulfite in which precipitation was effected with cadmium carbonate.

Comparing the experiments on detaching polysulfide sulfur by means of various additives, we can set up the following order of sulfur-detaching ability:

$$CN' > SO_3'' > AsO_3'''.$$

The method we used did not make it possible to obtain data on the kinetics of the reaction under investigation, as the results of analyses give, so to speak, an instantaneous conversion, with an extremely negligible growth during subsequent prolonged interaction.

4. Quantitative Determination of the Detached Sulfur in Viscose

(Experimental work by S. N. Danilov and N. M. Grad)

Since a dixanthide is formed when cellulose xanthate is oxidized by atmospheric oxygen, in a viscose, especially in an overripe viscose, in which only little free alkali remains, so that the concentration of the latter is not enough to cleave the cellulose dixanthide, the latter may contain sulfur and yield it up to potassium cyanide, being converted into a thioanhydride, which is more easily cleaved by an alkali. The older the viscose, the more likely it will contain cellulose dixanthide, which can surrender one atom of sulfur to potassium cyanide, like the perthiocarbonate, the disulfide, and the thiosulfate. This is why allowance must be made for the cellulose dixanthide in a complete accounting of the viscose substances that can yield up sulfur to potassium cyanide. The cleavage of dixanthides by sodium sulfide is the origin of the disulfides formed within the viscose, as has been pointed out above in our discussion of the action of sodium sulfide upon a dixanthide.

As has been pointed out already, cyanides can detach sulfur from other compounds in the cellulose besides the cellulose disulfide: sodium perthiocarbonate, sodium disulfide, and sodium thiosulfate.

a) Method of analysis. The customary iodometric titration of viscose in an acetic acid medium and in a mineral acid medium to determine the sulfur combined as a xanthate and in by-products provides a notion of the quantity of xanthate and trithiocarbonate sulfur. Analysis of the viscose with the carbon disulfide and the hydrogen sulfide driven out of the viscose (Bernhardt method), to which a mineral acid has been added, likewise yields data on the presence of xanthate groups and the trithiocarbonate, but it is useless, like the first method, whenever the viscose contains appreciable quantities of sulfite or other sulfur-containing compounds. Of greater service in determining the various sulfur-containing substances in viscose are the customary variants of precipitation of carbon disulfide derivatives and of the trithiocarbonate and the xanthate by cadmium salts, which makes it possible to determine the sulfite and the thiosulfate in the solution. The method of potentiometric titration (Neiman, Kargin, and Fokina [16]) is satisfactory for determination of the sodium sulfide.

By means of a modification of the viscose analysis described by S. Danilov and S. Rizov [17], precipitation with cadmium salts (soluble salts, but possibly cadmium carbonate as well) is used after the free carbon disulfide has been determined. The carefully washed precipitate is analyzed iodometrically and by the Bernhardt method (trithiocarbonate, sodium sulfide, and dithio groups). We determine the sulfite and the thiosulfate in the filtrate in the usual manner. A more detailed analysis of of the precipitate and the filtrate can indicate the presence of other compounds as well. Supplementary analyses are required, however, to determine the polysulfide substances. The cyanide method is the best method for determining the substances that can yield up atoms of sulfur, i.e., that belong to the group of disulfide compounds. We developed various modifications to determine such substances. A solution of potassium cyanide was added to the viscose, and 24 hours later the quantity of thiocyanogen was determined, and from this the quantity of sulfur detached from the perthiocarbonate, the disulfide, etc.; this latter is ½ or ¼ of the total sulfur contained in these substances. To determine the quantities of thiocyanogen

the xanthate and the by-products (sulfide, trithiocarbonate) are precipitated with lead acetate or as cadmium salts. The filtrate containing CN', CNS', SO_3'', and S_2O_3'' is analyzed in the usual manner.

These variants of the methods of analysis for determination of the sodium perthiocarbonate and disulfide possess the following disadvantages:

1) An excess of precipitant must be avoided when precipitating with lead acetate, since lead thiocyanate is soluble when the solution contains 2.5-3% of free alkali, and an excess of lead acetate can cause the thiocyanate to appear in the precipitate;

2) The method employing lead salts is useless when the SO_3'' and S_2O_3'' ions must be determined in the filtrate;

3) When cadmium salts are employed, neither cadmium nitrate nor cadmium sulfate can be used because of the possibility of partial decomposition of the SO_3'' and the S_2O_3''; cadmium carbonate is more suitable, although its insolubility gives rise to some inconveniences.

More reliable data are obtained when cobalt salts are used. It is known that the cobaltic cyanides are insoluble, in contradistinction to the soluble thiocyanates, which makes it possible to titrate the thiocyanate in the solution back with silver nitrate in the presence of ammonium ferric alum as an indicator until the blood-red solution is decolorized. We found that the presence of the ions of sulfuric and sulfurous acid in the solution does not interfere with the determination of the thiocyanogen ion.

In practice, we effected determination of the thiocyanogen ion in the following manner. A solution of potassium cyanide was added to a solution of the dixanthide or viscose under investigation. Twenty-four hours later a slight excess of cobalt nitrate was added to the reaction mixture, the reaction mixture was stirred with a stirring rod, and after a small interval of time the black precipitate of cobalt sulfide compounds (potassium cobalt is a chocolate-colored precipitate) and the coagulated xanthate were filtered out. After the precipitate had been washed repeatedly with water, and these wash waters had been added to the filtrate, the solution produced was tinted pink very faintly (owing to the presence of cobalt ions). Checking the completeness of precipitation of the sulfide compounds and of the unreacted cyanogen (qualitative test of a few drops of filtrate for the absence of precipitate when a cobaltic salt is added), a few drops of ammonium ferric alum were added to the filtrate, turning it blood-red if a thiocyanate is present. Then the solution is subjected to Volhard titration with silver nitrate until the color due to the presence of a coordination iron thiocyanate compound in the solution above the silver thiocyanate precipitate disappears. The quantity of sulfur converted into the thiocyanate is determined from the amount of silver nitrate used up in the titration.

When a large excess of cobalt nitrate is used, the filtrate is colored an intense pink owing to the high concentration of cobalt ions, which may interfere with determination of the instant at which the color is bleached out during the titration. In such a case the determination may be made as follows. An excess of silver nitrate is added to the solution of cobalt thiocyanate. The silver thiocyanate formed is filtered out and washed with hot water until the wash waters are completely colorless; the precipitate can then be returned, together with the filter, to the beaker in which the silver-nitrate precipitation took place, and reprecipitated with a 5% solution of sodium chloride heated almost to the boiling point for 3-5 minutes with vigorous stirring. After

filtering out the silver chloride thus obtained and washing it twice, the thiocyanogen ion is determined in the filtrate as sodium thiocyanate, and the silver nitrate is determined in the presence of ammonium ferric alum and a few drops of nitric acid.

In our determinations we had in front of us a calibrating standard consisting of a slightly pink solution of a cobalt salt, and we titrated the silver nitrate with ammonium ferric alum without removing the cobalt, since the difference between the color of the solution due to the presence of cobalt and that of the thiocyanogen-iron coordination compound was great enough to be detected at a glance.

This reaction likewise enabled us to make a rapid qualitative determination of the presence or absence of the thiocyanogen ion in the viscose by adding a cobalt salt to the reaction mixture, filtering out the precipitate, and adding a few drops of ferric chloride to the filtrate. The cobalt also removes any excess of alkali in the viscose, which would interfere with the reaction between the iron and the thiocyanogen. The solution's turning red indicates the presence of thiocyanogen.

In order to ascertain the sensitivity of the method of determining thiocyanogen sulfur in viscose solutions (after precipitation with cobalt) when the SO_3" and S_2O_3" ions may be present, we performed the following experiment. Potassium thiocyanate was desiccated to constant weight at a temperature of 120°. We added the following reagents to 100 ml of water: a) 0.25 g of potassium thiocyanate; b) 0.2 g of potassium cyanide; c) 0.2 g of sodium sulfite; and d) 0.2 g of sodium thiosulfate.

In one of the runs we likewise added 0.2 g of sodium sulfate. 6 ml of a 1N solution of cobalt nitrate (containing 92 g of $Co(NO_3)_2$ per liter) was added to the reaction mixture of the foregoing reagents. After a few minutes had passed the precipitate formed was filtered out, and the completeness of the cyanogen's precipitation was checked. A few drops of ammonium ferric alum were then added to the pale-pink filtrate, which was then titrated back with silver nitrate until the dark-red coloring disappeared. For the sake of brevity we shall leave out the results of this determination, which indicate that the precision of measurement is $\pm 0.5\%$.

We believe that this method possesses the following advantages when employed for viscose:

1) Adequate sensitivity in determining the thiocyanogen formed.

2) Simplicity of treatment of the reaction mixture, making it possible to determine the thiocyanogen formed, qualitatively as well as quantitatively, by a single-stage precipitation of the sulfur products and the unreacted cyanide.

3) The disulfide sulfur in the cellulose derivative as well as in the by-products of the disulfide type can be determined by separate treatment of the main and by-products of the viscose, since the cobalt salt precipitates the xanthate, a number of sulfur compounds, and cyanogen, and eliminates the alkali.

4) The presence of small amounts of SO_2" and S_2O_3" ions in the filtrate does not interfere with the determination of the thiocyanogen by the method described above.

A disadvantage of the method is the fact that the red coloring due to the iron clashes with the pink color of the cobalt when the amount of thiocyanogen present is small; this may make determination of the transition point somewhat difficult during titration. But as we have already pointed out, this transition

is instantaneously observable by the naked eye with adequate sharpness, even at low concentrations of the thiocyanogen ion.

b) Determination of the thiocyanogen ion when cyanides are added to the viscose. For these tests we prepared a viscose characterized by the following parameters: ripeness (as measured by ammonium chloride); viscosity: 38 (as measured by the time required for a metal ball weighing 0.133 g to penetrate a layer of viscose 20 cm thick); alkalinity: 7.01; and alpha cellulose content: 6.4%.

1) A solution of 0.4 g potassium cyanide in 25 ml of water was added in the cold to 20 g of freshly prepared viscose. Twelve hours later, the sulfur by-products of a sulfide nature, the unreacted cyanide, and the cellulose xanthate were precipitated from part of the viscose solution by a 1.0N solution of cobalt nitrate(by the method we have developed). We reacted the filtrate with a solution of ferric chloride. The absence of any red coloring, which would have indicated the formation of the thiocyanogen ion, showed that no thiocyanogen is formed when potassium cyanide reacts with freshly prepared viscose. Repetition of this experiment with another viscose, likewise freshly prepared, confirmed this result.

2) 100 g of the same viscose was set aside to stand in air, and subjected to the action of potassium cyanide after 4, 6, 7, and 8 days had elapsed (since the date on which the viscose had been prepared), after which it was subjected to the treatment described above. The outcome of these tests indicated that only after standing in air for 7 to 8 days does viscose form appreciable quantities of thiocyanate when reacted with potassium cyanide; we detected the thiocyanate by the red coloring produced when the filtrate obtained after several interfering products had been precipitated with a cobalt salt was reacted with salts of trivalent iron.

3) Three 20-g batches of freshly prepared viscose were set aside to stand for 10 days—the first one with no additive, the second with potassium cyanide added, and the third with sulfite added. We observed the changes of color in the viscose under the influence of these additives and with time (Table 10).

4) After the xanthate had been coagulated with methanol, potassium cyanide was added tc the yellow (alcoholic) solution of the by-products of the freshly prepared viscose. The color of the solution did not change and no thiocyanate was formed even after 10 days had passed.

5) In the viscose that produced thiocyanogen when treated with potassium cyanide, the xanthate was coagulated with methanol, the yellow alcoholic solution of the by-products was treated with potassium cyanide, and thiocyanogen was detected in the filtrate after the main products had been precipitated with cobalt (although the filtrate did not turn pink when it was reacted with potassium cyanide).

In subsequent tests we made a quantitative determination of the thiocyanogen formed when viscose is reacted with potassium cyanide.

Quantitative determinations of the thiocyanate formed in viscose were made with a viscose of the following parameters: viscosity:32; ripeness:33 (as measured by ammonium chloride); alkalinity:6.52; alpha cellulose content:7.4% and sulfur content:2.37%.

The viscosity and ripeness of the viscose had changed as follows after a few days had elapsed: ripeness:6 (as measured by ammonium chloride); viscosity: 41.

TABLE 10

Test no.	Viscose additives	Change in viscose color	Time that color changed	Quantitative analysis of filtrate
1	No additive .	No change	After 10 days	—
2	KCN.	Changes to rose-orange	Within 2 days	Thiocyanogen appeared after 7 days
3	Na_2SO_3. . . .	Turns pink, but paler than in Experiment 2	Within 7 days	Thiosulfate from the very beginning

a) A weighed batch of viscose (ripeness 6) was used. To it we added a solution of 3 g of potassium cyanide. Two days later the color of the viscose had changed from yellow to orange-pink. Then cobalt nitrate was added, and the black precipitate that formed was filtered out half an hour later. A small quantity of ammonium ferric alum was added to the pale-pink filtrate, after which the solution was titrated with silver nitrate until it regained its initial pink color above the precipitate, i.e., until the color due to the thiocyanogen-iron coordination compound had vanished.

Weight of viscose: 38.5882 g.

Silver nitrate used in titration: 30.8 ml ($T_{AgNO_3/CNS}$=0.016938).

Amount of sulfur transferred into thiosulfate: 0.0984 g.

Total disulfide sulfur: 0.0984 X 4 = 0.3936 g.

Percentage of disulfide sulfur in viscose: 1.02%.

To ascertain whether the sulfur (that constitutes the thiosulfate) is detached by the potassium cyanide solely from the sulfurized by-products, or the cellulose derivative, cellulose dixanthide, may also participate in this process of sulfur transfer, we ran the following two experiments in parallel with the above, using the same viscose.

b) After the viscose had been carefully neutralized with half-normal acetic acid, the cellulose derivatives (the xanthate and the dixanthide) were precipitated from the viscose with ethyl alcohol by the Atsuki method, and the precipitate was filtered out and washed several times with alcohol and ether. Then the cellulose derivatives produced were shaken up in water, though full dissolution was not obtained. A solution of 3 g of potassium cyanide was added to the suspension produced, and the thiocyanate formed was determined as in the preceding experiment after the passage of two days, during which no change in the color of the initial solution was observed.

Weight of viscose: 39.8431 g.

Silver nitrate used in titration: 24.8 ml ($T_{AgNO_3/CNS}$=0.016938

Amount of sulfur transferred to thiosulfate: 0.0792 g.

Total sulfur in the dixanthogenide: 0.0792 X 4 = 0.3168 g.

Percentage of dixanthogenide sulfur in viscose: 0.79%.

c) The xanthogenate was coagulated from the viscose by methanol, the coagulated xanthogenate being triturated several times in a mortar with new batches of alcohol to effect more complete dissolution of all the by-products in the alcohol. Treatment with methanol was continued until the methanol recovered after treatment of the xanthogenate was completely colorless. A solution of 3 g of potassium cyanide was likewise added to the yellow solution of the sulfur by-products in methanol. Two days later, the color of the solution not having changed in the interim, as is observed when potassium cyanide reacts with viscose, the reaction mass was treated as described previously, the thiocyanate that formed being filtered out.

Weight of viscose: 39.8699 g

Silver nitrate used in titration: 5.6 ml ($T_{AgNO_3/CNS} = 0.016938$).

Amount of sulfur transferred to thiosulfate: 0.0895 g

Total sulfur (assuming it is chiefly in perthiocarbonate form):
0.0169 X 4 = 0.0677 g.

Percentage of perthiocarbonate sulfur in viscose: 0.17% (or assuming it is in disulfide form: 0.0169 X 2 = 0.0338, or 0.08%).

Similar experiments made with another viscose yielded the following results (Table 11).

TABLE 11

	Total quantity in viscose	In cellulose derivatives	In by-products	Remarks
1. Weighed batch of viscose, g	24.4652	22.5408	18.4103	
2. Amount of silver nitrate required for titration, ml . . .	17.7	11.7 ($T_{AgNO_3/CNS}$, 0.005878)	3.1	
3. Amount of sulfur transferred to thiocyanogen ion, g	0.0574	0.0360	0.0101	
4. Total sulfur in disulfide compounds, g	0.2296	0.1442	0.0405	The figures in Column 4 were secured by multiplying the values in Par. 3 by 4.
5. Percentage of sulfur in disulfide form	45.02 100%	30.35 67.44%	10.43 23.20%	

SUMMARY

1. Viscose contains polysulfurized products, such as : sodium disulfide, sodium thiosulfate, and cellulose dixanthide.

2. The formation of thiocyanate when a cyanide is added to viscose (the

cyanide method) is a characteristic reaction for polysulfurized substances; similarly, sodium sulfide is converted into sodium thiosulfate, and sodium arsenite is converted into sodium thioarsenate.

3. Lead salts or, better yet, cadmium salts may be used to determine the carbon-disulfide derivatives; particularly useful for this analysis are the salts of cobalt. These methods of analysis make it possible to determine the sodium sulfite and thiosulfate, as well as the cyanide and thiocyanate, making a correction for sodium chloride, using the customary procedures of analytical chemistry.

4. When sodium sulfide is reacted with cellulose dixanthide (as a suspension), cellulose xanthate and sodium disulfide and sulfate are formed; if sodium sulfite is added to a suspension of diethyldixanthide, thiosulfate is found, in addition to the xanthate, but no thioanhydride is detected.

5. As the viscose ripens, substances accumulate in it that can yield up their sulfur atom, so that the addition of a cyanide (potassium or sodium) to the viscose as it ripens increases the quantity of thiocyanate to be titrated back. Similarly adding sodium sulfite to the viscose increases the amount of thiosulfate. If the sulfite and the cyanide are added to the viscose simultaneously, the amount of thiocyanate rises, while the percentage of sodium sulfite increases and the amount of the thiosulfate diminishes. Moreover, sodium thiosulfate is not the sole source of the thiocyanate when a cyanide is added to viscose.

6. When a cyanide is added to viscose, the percentage of sodium sulfide in the latter rises, and the percentage of trithiocarbonate drops. Sodium sulfide added to viscose gradually disappears, but adding sodium sulfite retards the disappearance of the sodium sulfide.

7. The behavior of sodium cyanide, sulfite, and arsenite toward sodium disulfide was explored. It was found that sodium disulfide yields up a sulfur atom to a cyanide most readily; sodium sulfite comes next. The addition of cadmium salts facilitates the addition of sulfur to a cyanide, sulfite, or arsenite, forming sodium thiocyanate, thiosulfate, and thioarsenate, respectively.

8. A thorough investigation was made of the substances found in viscose as it ripens that are capable of yielding up an atom of sulfur to sodium (potassium) cyanide, using the cobalt-salt method. It was shown that a thiocyanate is formed in old viscoses: 1) from the cellulose dixanthide, the reaction between the cyanide and the dixanthide taking place extremely quickly; 2) owing to the accumulation of sodium sulfide and, apparently, sodium perthiocarbonate and thiosulfate in viscose, as is shown by analysis of the filtrate after the cellulose xanthate has been coagulated.

9. The value of the method of viscose analysis by means of salts of hydrocyanic acid to ascertain the percentages of its substances that can yield up an atom of sulfur has been demonstrated. Similarly, sodium sulfite and arsenite are converted into sodium thiosulfate and thioarsenate, respectively, but these reactions are less useful than the cyanide reaction in ascertaining the sulfur-yielding substances in viscose. Addition of sodium cyanide, sulfite, and arsenite may, however, partially change the composition of the viscose, facilitating the increase of sodium sulfide within it at the expense of the sodium trithiocarbonate.

10. The problem of the accumulation of sulfur-containing compounds during the xanthation of alkali cellulose and during the ripening of viscose has been explored.

The reaction of carbon disulfide with caustic soda takes place via a dithiocarbonate, which is hydrolytically cleaved by caustic soda into a monothiocarbonate, which in turn gives rise to sodium sulfide, soda, and possibly, carbonyl sulfide. The action of neutral sodium sulfide or acid sodium sulfide upon a dithiocarbonate gives rise to the trithiocarbonate, which then hydrolyzes to form sodium sulfide and soda.

The hydrolytic cleavage of cellulose xanthates by caustic soda is accompanied by the formation of dithiocarbonates whereas the hydrolytic action of sodium sulfide or sodium hydrosulfide makes for the direct formation of the trithiocarbonate. The hydrolytic cleavage of cellulose xanthates by various alkaline agents requires further study.

11. The amount of carbon disulfide, which is unable to yield an atom of sulfur to potassium cyanide according to our experiments, in viscose still requires confirmation by further experimentation.

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THE SYNTHESIS AND CONVERSIONS OF TERTIARY ALIPHATIC-AROMATIC ALCOHOLS OF THE ETHYLENE SERIES

I. SYNTHESIS OF METHYLPHENYLVINYLCARBINOL AND METHYLBENZYLVINYLCARBINOL

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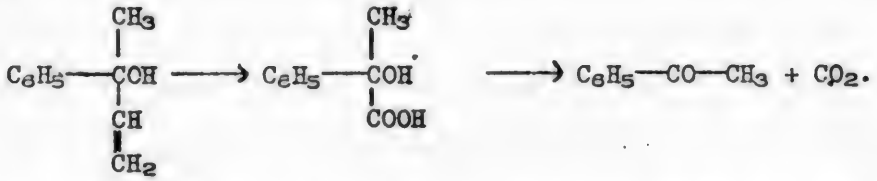
Academician A. E. Favorsky Laboratory of the A. A. Zhdanov
Leningrad State University, awarded the Order of Lenin

An original method of synthesizing tertiary alcohols of the ethylene series was developed by Academician A. E. Favorsky and his associates. The raw materials for the Favorsky synthesis of ethylene alcohols are ketones and acetylene. The acetylenylcarbinols [1,2] synthesized by the reaction between the ketone and the acetylene (in the presence of powdered potassium hydroxide) are hydrogenated electrolytically under certain conditions to the corresponding vinylcarbinols [3,4,5]. It was noticed that the synthesis of acetylenylcarbinols from a ketone and acetylene is effected smoothly with satisfactory yield when aliphatic ketones are involved. Some aliphatic-aromatic ketones behave differently in this reaction. In particular, acetophenone hardly reacts at all with acetylene. Though Carothers [6] reports that he succeeded in producing methylphenylacetylenylcarbinol (3-phenylbutyn-1-ol-3) by reacting acetylene with acetophenone in the presence of sodium amide, the yield of methylphenylacetylenylcarbinol in this reaction did not exceed 2% of the theoretical. The efforts of A. E. Favorsky to synthesize methylphenylacetylenylcarbinol from acetophenone and acetylene in the presence of powdered caustic potash were fruitless. In some of the experiments a mixture of ether and benzene was used instead of the ether solution in order to raise the temperature of the reaction mixture. But here, too, almost all the acetophenone was recovered unreacted after the reaction. The research of A. I. Zakharova [7] showed that benzophenone reacts with acetylene in the presence of powdered caustic potash, the yield of diphenylacetylenylcarbinol being as much as 30% and even 50% of the theoretical. But it is fairly hard to separate the diphenylacetylenylcarbinol formed in the reaction from its mixture with benzophenone and the reaction by-product, tetraphenylbutynediol. That is why we resolved to synthesize aliphatic-aromatic ethylene alcohols directly by the action of the corresponding organomagnesium compounds upon unsaturated ketones, instead of from acetylenic alcohols. In this way we produced methylphenylvinylcarbinol (3-phenylbuten-1-ol-3) by reacting phenylmagnesium bromide with methyl vinyl ketone, and methylbenzylvinylcarbinol by reacting benzylmagnesium bromide with the same ketone.

The methylphenylvinylcarbinol was completely identified by determining its molecular weight, its refractive index, its carbon and hydrogen percentage (Liebig method), and its hydroxyl groups (Chugayev-Tserevitnikov method). Oxidation of the methylphenylvinylcarbinol by an aqueous solution of permanganate in the cold yielded acetophenone and oxalic acid. The initial rection

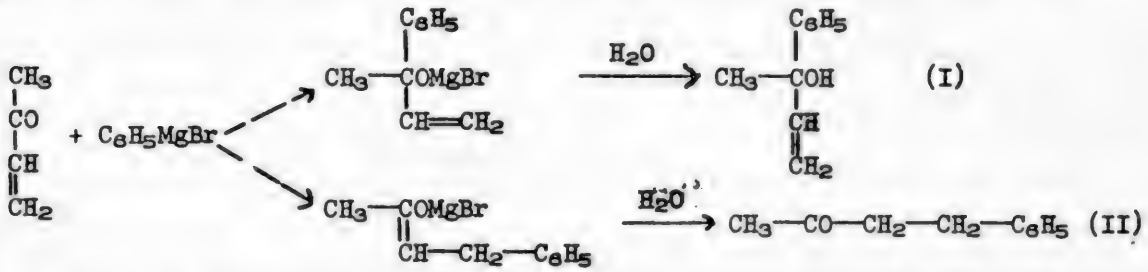
product is probably atrolactic acid, which readily oxidizes further to acetophenone.



The presence of oxalic acid in the oxidation products might lead one to assume that this reaction would yield the primary γ, γ-methylphenylallyl alcohol instead of the tertiary alcohol, methylphenylvinylcarbinol. We therefore ozonized the methylphenylvinylcarbinol and then hydrogenated it catalytically. The ozonide was decomposed by heating it with water. Acetophenone, formic acid, benzoic acid, and tracesof atrolactic acid were identified in the aqueous solution. No oxalic acid was found. Catalytic hydrogenation of methylphenylvinylcarbinol with hydrogen over platinum black yielded a saturated tertiary alcohol, methylethylphenylcarbinol. Methylbenzylvinylcarbinol was identified by determining its molecular weight, its refractive index, and its percentages of carbon and hydrogen (by the Liebig method). No compound other than benzoic acid could be identified when the methylbenzylvinylcarbinol was oxidized with an aqueous solution of permanganate.

In synthesizing methylphenylvinylcarbinol (I) and methylbenzylvinylcarbinol we observed the formation of other saturated ketones: benzylacetone (II) and 1-phenylpentanone-4.

Kohler [8] was the first to establish the fact that when an organomagnesium compound is reacted with unsaturated ketones, two reactions take place simultaneously: on the one hand, the organomagnesium compound acts on the carbonyl group of the unsaturated ketone, resulting in the formation of an unsaturated alcohol; on the other hand, the organomagnesium compound is added to the unsaturated compound at the 1,4 position, resulting in the formation of saturated ketones. According to Kohler, the following reactions should take place when phenylmagnesium bromide reacts with methyl vinyl ketone:



In fact, we synthesized benzylacetone together with methylphenylvinyl carbinol, and 1-phenylpentanone-4 together with methylbenzylvinylcarbinol, the yield of the saturated ketones equalling that of the unsaturated alcohols in some tests. The ketones were identified by synthesis of their semicarbazones. The semicarbazone of benzylacetone fused at 141-142° and exhibited no depression with a known sample of benzylacetone semicarbazone. The semicarbazone of 1-phenylpentanone-4 fused at 135-136° after recrystallization from ethyl alcohol. Diels [8] gives a m.p. of 125° for the semicarbazone of 1-phenylpentanone-4 recrystallized from methanol. But, if we start with Kohler's reaction

it is hard to conceive of the formation of any other ketone than 1-phenylpentanone-4. A determination of the percentage of nitrogen in the semicarbazone with a m.p. of 135-136° proved to us that this was the semicarbazone of phenylpentanone.

We propose later on, to synthesize other homologues of the aliphatic-aromatic ethylenic alcohols from methyl vinyl ketone and some other unsaturated ketones and the respective arylmagnesium bromide, and then to investigate the action of sulfuric acid on these alcohols under various conditions.

EXPERIMENTAL

Synthesis of Methylphenylvinylcarbinol

53 g of methyl vinyl ketone in 100 ml of ether was added in the cold and with constant stirring to phenylmagnesium bromide, prepared in the usual manner from 18 g of magnesium shavings and 120 g of bromobenzene. Decomposition was effected with water, a saturated solution of ammonium chloride, or a 50% solution of caustic potash. The yield hardly changed, no matter what decomposition agent was employed.

The ether extract was treated with a solution of sodium bisulfite (30 g of bisulfite in 45 ml of water) to eliminate the ketone, and then with a solution of caustic potash to decompose the residual bisulfite and to remove the traces of phenol formed in the reaction, after which it was desiccated over fused potash. After the ether had been driven off, we got 15.1 g of a product that boiled at 92-95° (7mm), and 33 g of tar. Another fraction, boiling at 97-112° (10 mm), totaling some 5 g, was secured without any bisulfite treatment.

Analysis of the 92-95° (7 mm) Fraction

Combustion of the product obtained indicated that the methylphenylvinylcarbinol formed in the reaction was contaminated with diphenyl. To eliminate the diphenyl, the carbinol was subjected to partial steam distillation; this eliminated some of the carbinol and almost all the diphenyl. The carbinol thus purified distilled, in the main, at 89-90° (5 mm).

Analysis of this fraction yielded the following results:

$d_4^{21.1}$ 0.9965; $n_K^{21.1}$ 1.52772.

Found: MR_K 45.80

$C_{10}H_{12}O$ F_4. Calculated: MR_K 45.50

0.1172 g substance: 0.3495g CO_2; 0.0844 g H_2O.

0.1104 g substance: 0.3286 g CO_2; 0.0807 g H_2O.

Found %: C 81.30, 81.19; H 8.06, 8.12.

$C_{10}H_{12}O$. Calculated %: C 81.02; H 8.17.

0.4008 g substance; 19.70 g benzene: Δt 0.692°.

Found: M 150.9

$C_{10}H_{12}O$. Calculated: M 148.0

0.1566 g substance: 23.5 ml CH_4 (19°, 764.5 mm).

Found %: OH 10.70.

$C_{10}H_{11}OH$. Calculated %: OH 11.50.

All these figures indicate that we synthesized methylphenylvinylcarbinol or 3-phenylbuten-1-ol-3.

Catalytic hydrogenation of methylphenylvinylcarbinol. We took 6.8 ml of methylphenylvinyl carbinol, boiling at 95-98° (10 mm), in 45 ml of absolute alcohol for hydrogenation. To this solution we added 1.5 g of platinum black (Gutbier and Maisch [10]). Hydrogenation and saturation of the catalyst required 1350 ml of hydrogen (for technical reasons, the saturation and the hydrogenation were done together). Then the addition of hydrogen was stopped completely. After the alcohol had been driven off, a product was distilled that did not bleach an aqueous solution of permanganate; the following fractions were secured:

Fraction I: 81-85° (5 mm) . . . 2.0 g

Fraction II: 85-88° (5 mm) . . . 3.1 g.

Fraction II was redistilled at normal pressure in the 210-214° temperature range.

d_4^{17} 0.9497; n_K^{17} 1.48692.

	Found:	MR_K 45.42
$C_{10}H_{14}OF_3$.	Calculated:	MR_K 45.99

The boiling point of methylethylphenylcarbinol is given as 211-212°. Hence, the catalytic hydrogenation of methylphenylvinylcarbinol gave us methylethylphenylcarbinol.

Oxidation of methylphenylvinylcarbinol with an aqueous solution of permanganate. 9.8 g of methylphenylvinylcarbinol was oxidized with the calculated quantity of permanganate (35 g). The distillate of neutral products contained an oil, which was extracted with ether. After the ether had been driven off, we got 1.3 g of a substance with the characteristic odor of acetophenone. The semicarbazone prepared from this substance fused at 196-197°. A test sample mixed with known acetophenone semicarbazone (m.p. 195-196°) fused at 196-197°. The residue left behind after the neutral products had been distilled off was acidulated with a calculated quantity of sulfuric acid and extracted with ethyl acetate. After the ethyl acetate had been driven off, there remained 0.5 g of crystals that fused at 97-100°. After repeated sublimation, the crystals fused at 187-188°. A test sample mixed with oxalic acid fused at 187-188°. The acid residue was extracted for a long time with ether in a percolator. Driving off the ether yielded 0.3 g of an acid that had a very broad melting-point range. The acid was then fractionated. The first fraction fused at 190°, the last at 102-105°. The residue of approximately 0.1 g did not sublime, but fused at 92-95°. It is possible that this was atrolactic acid, whose melting point is given as 93-94° in the literature [11].

Ozonation of methylphenylvinylcarbinol. 4.7 g of methylphenylvinylcarbinol was treated with 4% ozone in 50 ml of chloroform. After the chloroform had been driven off in vacuum, the ozonide was heated with water for 8 hours. The neutral products were then driven off from the water, which had been neutralized with soda. The aqueous distillate which contained drops of oil, was extracted with ether. Driving off the ether yielded 2.1 g of a substance that formed a precipitate with semicarbazide. The melting point of the semicarbazone was 194-195° (from alcohol). The melting point of a test sample mixed with acetophenone semicarbazone was 195-196°.

The residue left after the neutral products had been driven off was evaporated down to very small volume and then acidulated with sulfuric acid; this caused 0.5 g of crystals to settle out, which fused at 120-121° after sublimation. The melting point of a test sample mixed with benzoic acid was 120-121°.

After the precipitated benzoic acid had been removed, the solution was extracted with ether by shaking in a separating funnel. After the ether extract had been dried with magnesium sulfate and the ether had been removed, we got 2.4 g of a substance. Distillation yielded the following fractions:

I. -65-100° . . . . . 0.9 g

II. 100-104° . . . . . 1.2 g.

The sclid residue left in the flask weighed 0.08 g.

Fraction II had a sharp odor and formed a precipitate of calomel when treated with mercuric chloride; the silver salts of this acid turned black quickly. All this points to the presence of formic acid. The solid residue in the flask fused at 117°. A test sample mixed with benzoic acid fused at 117-120°. Then the acid solution was extracted with ether for a long time in a percolator. The usual drying and extraction of the ether yielded 0.35 g of a liquid that gave the qualitative reaction for formic acid (with mercury chloride). All the acid evaporated when it was left to stand in a vacuum exsiccator over sulfuric-acid. Thus, ozonation yielded acetophenone, formic acid, and a small amount of benzoic acid.

Titration of methylphenylvinylcarbinol with an aqueous solution of bromide-bromate. The methylphenylvinylcarbinol was titrated in the usual manner, but each batch of the carbinol was dissolved in 100 ml of ethyl alcohol instead of in water (see Table).

Weight of substance g	Br found, g	Br computed, g	Addition in per cent of the theoretical
0.2162	0.2108	0.2334	90.28
0.2444	0.2343	0.2634	88.94

Investigation of the 97-112° (10 mm) Fraction

The semicarbazone was prepared in the usual manner from 1 g of the fraction that distilled at 97-112° (10mm). After a brief shaking in the cold, an abundant precipitate of the semicarbazone settled out; after recrystallization from alcohol it fused at 141-142°. To produce the semicarbazone of benzyl acetone, we took 2 g of benzylidene acetone and hydrogenated it catalytically in an alcoholic solution over platinum black. Driving off the alcohol yielded 1.5 g of benzyl acetone, whose semicarbazone fused at 141-142° after crystallization from alcohol. A mixed test sample likewise fused at 141-142°. Hence, Fraction IV consisted chiefly of benzyl acetone.

Synthesis of Methylbenzylvinylcarbinol

22 g of methyl vinyl ketone in 200 ml of absolute ether was added to an ether solution of benzylmagnesium bromide, prepared from 10 g of magnesium shavings and 78 g of benzyl bromide. Decomposition was effected with water acidulated with acetic acid. In some of the experiments water or a 50% solution of caustic soda was used to effect decomposition. The yield of methylbenzylvinylcarbinol remained about the same no matter what agents were used to decompose the organomagnesium coordination compound. Driving off the ether yielded 13 g of a product that boiled at 103-115° (10mm); the second fraction (9 g) distilled at 115-134° (10 mm). 27 g of tar remained in the distilling flask. Repeated distillation was used to isolate a substance with a boiling point of 98-100° (9 mm) from the first fraction. This substance did not react with semicarbazide, but quickly bleached an aqueous solution of permanganate in the cold.

d_{18}^{4} 0.9954; n_{α}^{18} 1.52568.
Found: MR_{α} 49.85
$C_{11}H_{14}OF$ Calculated: MR_{α} 50.09
0.2120 g substance: 17.41 g benzene: Δt 0.380°
0.1858 g substance: 19.49 g benzene: Δt 0.300°
Found: M 164.4, 160.3.
$C_{11}H_{14}O$. Calculated: M 162.

Analysis of the 115-134° (10 mm) fraction. We prepared the semicarbazone of the fraction with a boiling range of 115-134° (10 mm). The melting point of the semicarbazone was 135-136° after recrystallization from ethyl alcohol.

0.0635 g substance: 10.3 ml N_2 (15°, 767.5 mm).
0.0785 g substance: 12.9 ml N_2 (17°, 760.9 mm).
Found %: N 19.17, 19.07.
$C_{12}H_{17}ON_3$. Calculated %: N 19.17

The percentage of nitrogen corresponded to the value computed for phenyl pentanone semicarbazone.

50 g of the second fraction, secured from several runs, was agitated for 5 hours in 150 ml of ether with a 40% solution of bisulfite. After the precipitated bisulfite compound had been filtered out, and the ether solution washed with soda and then dried, the ether was driven off, and the residue was distilled in vacuum. The following fractions were collected:

I 116-120° (22 mm). . . . . 8.8 g
II 120-124° (22 mm). . . . .14 g
III 124-131° (22 mm). . . . .10.3 g

Fraction II was analyzed. It did not react with semicarbazide.

d_{4}^{18} 0.9938; n_{α}^{18} 1.52411.
Found: MR_{α} 49.84.
$C_{11}H_{14}OF_4$. Calculated: MR_{α} 50.09.
0.1119 g substance: 0.3334 g CO_2; 0.0888 g H_2O.
0.0997 g substance: 0.2967 g CO_2; 0.0795 g H_2O.
Found %: C 81.25, 81.16; H 8.88, 8.92.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

These figures correspond to those computed for methylbenzylvinylcarbinol.

Oxidizing methylbenzylvinylcarbinol with an aqueous solution of permanganate. 6 g of methylbenzylvinylcarbinol was oxidized with an aqueous solution of a calculated quantity (19.5 g) of permanganate. The substance oxidized very quickly, and we had to cool the mixture externally with ice water. The solution obtained after the manganese dioxide had been filtered out was steam distilled; we were unable to detect any neutral products (with p-nitrophenylhydrazine). When the solution was acidulated, a large quantity of solid acid was thrown down; it fused at 120° after crystallization from water. A test sample mixed with benzoic acid fused at 120.5°. No other acids were found.

SUMMARY

1. A tertiary ethylenic alcohol not described in the literature,

methylphenylvinylcarbinol, was synthesized by reacting phenylmagnesium bromide with methyl vinyl ketone and then identified.

2. The reaction of benzylmagnesium bromide with methyl vinyl ketone produced methylbenzylvinylcarbinol, likewise not described in the literature.

3. It has been shown that in both instances saturated ketones: benzyl acetone and 1-phenyl pentanone-4, are synthesized alongside the tertiary ethylenic alcohols.

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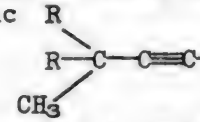
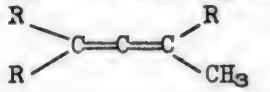
INTRAMOLECULAR REARRANGEMENTS IN THE ACETYLENE SERIES

V. REACTIONS OF THE ACETYLENIC CHLORIDE-3-CHLORO-3-METHYL-HEXYNE-4 - WITH ORGANOMAGNESIUM COMPOUNDS

A. I. Zakharova

Chair of Organic Chemistry. Faculty of Chemistry of the A. A. Zhdanov State University of Leningrad, awarded the Order of Lenin.

In one of our previous reports [1] we demonstrated that tertiary acetylenic chlorides that contain no free acetylenic hydrogen, of the type $(R)_2CCl-C\equiv C-R$, readily react with organomagnesium compounds. It was found that the course of the reaction depends upon the nature of the organomagnesium compound employed. Thus, when CH_3MgBr reacts with a chloride, a mixture of two hydrocarbons is formed: the acetylenic  representing the product

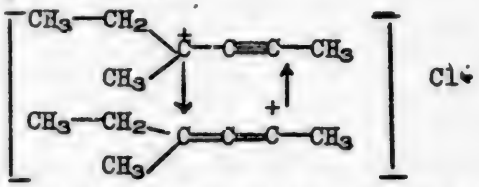
of the normal replacement of the radical of the organomagnesium compound by chlorine, and the allene structure  , the origin of which may be explained as due either to the subsequent isomerization of the normally formed acetylenic hydrocarbon or to the presence of an intramolecular rearrangement during the reaction. When the chloride is reacted with C_6H_5MgBr, the reaction is solely of the latter nature, i.e., nothing but a tetrasubstituted allene hydrocarbon is formed. The reaction conditions excluded the possibility of the first conjecture concerning the subsequent isomerization of the disubstituted acetylenic hydrocarbon to a tetrasubstituted allene. This led us to conclude that both of the hydrocarbons, the acetylene and the allene, are formed simultaneously and independently of each other. We also expressed an opinion concerning the probable mechanism of the reaction under investigation.

Continuing this research, we set as our goal the checking of these observations of ours (which, moreover, ran counter to the data in the literature on this problem [2]) on other compounds. With this in view we investigated the reactions of organomagnesium compounds (C_2H_5MgBr and C_6H_5MgBr) with a tertiary acetylenic chloride—3-chloro-3-methyl-hexyne-4 (I). Experiments showed that this reaction takes place very readily, with the evolution of heat; all the chloride enters into the reaction. The reaction of the chloride (I) with C_2H_5MgBr results in the production of a hydrocarbon that had a b.p. of 136-138°; after careful purification by distilling it over metallic sodium, did not exhibit the reaction for free acetylenic hydrogen, did not react with maleic anhydride, and turned orange with tetranitromethane. Oxidation of the hydrocarbon by a solution of $KMnO_4$ proved that it was nonhomogeneous. Methyl ethyl ketone, identified as the p-nitrophenylhydrazone, was isolated from the neutral oxidation products; the percentage of silver in the silver salts prepar-

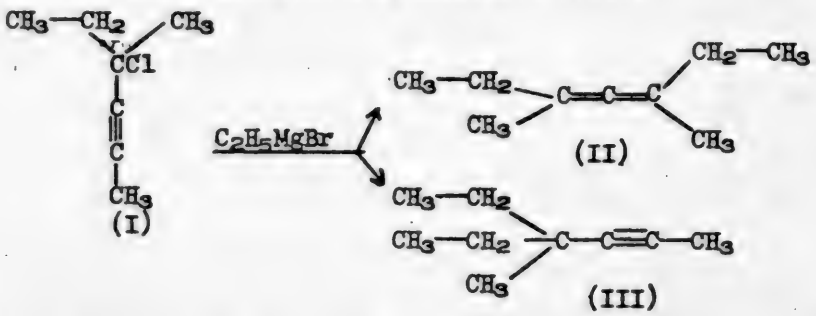
ed from the acid oxidation products corresponded to that of salts of acetic and methyldiethylacetic acids.

Determination of the elementary composition and the physicochemical constants of the hydrocarbon with a b.p. of 136-138°, and, more particularly, the synthesis of methyl ethyl ketone when it was oxidized, proved that it was a mixture of a tetrasubstituted allene—3,5-dimethylheptadiene-3,4 (II)—and a hydrocarbon of acetylenic structure—3-methyl-3-ethyl-hexyne-4 (III). The presence of the latter was proved by the production of acetic and methyldiethylacetic acids upon its oxidation.

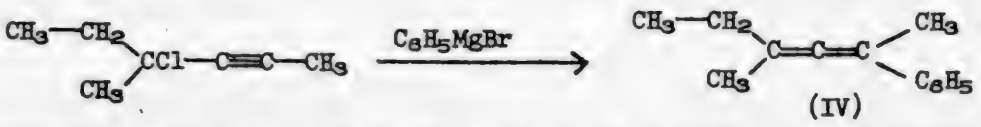
We effected the reaction between the chloride (I) and the C_2H_5MgBr under extremely mild conditions: in ether, with the temperature of the water bath not exceeding 40°. Under such conditions it is hard to see how subsequent isomerization of the products initially formed can take place. This is also supported by the statements in the literature on homologues of these hydrocarbons [3]. Because of this, we believe that in the present instance, as in the one discussed previously [1], the formation of an anomalous reaction product (II) is not due to subsequent isomerization of the acetylenic hydrocarbon normally formed (III), but that both hydrocarbons are formed simultaneously as the result of a rearrangement of the molecule at the instant the reaction occurs, apparently due to the formation of a restricted carbonium ion under the reacted conditions:



The presence of the latter ion in the reaction with the C_2H_5MgBr is also responsible for the formation of a mixture of two hydrocarbons: 3,5-dimethylheptadiene-3,4 (II) and 3-methyl-3-ethylhexyne-4 (III):



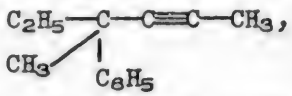
The reaction between the chloride (I) and C_6H_5MgBr was also explored. Here we were able to find only one anomalous reaction product: 3-methyl-5-phenylhexadiene-3,4 (IV):



This hydrocarbon had a b.p. of 94-95° at 7 mm; d_4^0 0.9402; d_4^{20} 0.9238; n_D^{20} 1.54359; n_α^{20} 1.53813; n_β^{20} 1.55780.

Oxidizing the hydrocarbon with an alkaline permanganate solution yielded methyl ethyl ketone and acetophenone. The same results were obtained when we analyzed the products of ozonizing the hydrocarbon. That is why we give it the structure (IV).

The fact that the products of the reaction between the chloride (I) and the C_8H_5MgBr did not include an acetylenic hydrocarbon:



which could have been produced if the normal reaction involving substitution of the C_8H_5 group for the chlorine atom had taken place, is due, apparently, to the hampering of the formation of this hydrocarbon by steric factors.

EXPERIMENTAL

1. Reaction of 3-Chloro-3-methylhexyne-4 With C_2H_5MgBr

The acetylenic tertiary chloride — 3-chloro-3-methyl-hexyne-4 (0.25 mole), prepared by reacting PCl_3 with methylethylmethylacetylenylcarbinol, as described by us previously [4], was added drop by drop, with constant stirring, to ethylmagnesium bromide, prepared in the usual manner and decanted from the residue of unreacted magnesium. A vigorous reaction set in at once. The dark solution of the organomagnesium compound gradually grew lighter, and a precipitate of the magnesium halide settled out. After all the chloride had been added, the reaction mixture was heated to 40° over a water bath and then decomposed with water and dilute hydrochloric acid. The ether solution was desiccated, and the ether was driven off. Fractionation of the reaction product into a 50-cm tower over metallic sodium yielded two main fractions. Fraction I—b.p. 107-108°—consisted of an unsaturated hydrocarbon, $CH_3-CH=C(CH_3)-C\equiv C-CH_3$, evidently formed detaching a hydrogen chloride molecule from the initial chloride. This hydrocarbon is also formed when 3-chloro-3-methylhexyne-4 (I) is synthesized from methylethylmethylacetylenylcarbinol by reacting the latter with gaseous hydrogen chloride; it was identified by us in our previous report [4].

Redistillation of Fraction II over metallic sodium yielded a hydrocarbon, whose analysis and the determination of whose constants gave the following results:

B.p. 136-138°; d_4^0 0.7929; d_4^{20} 0.7758; n_D^{20} 1.4478; n_α^{20} 1.4448; n_β^{20} 1.4560

Found: MR_D 42.75; MR_α 42.52; MR_β 43.44.

C_9H_{16} F_2. Calculated: MR_D 42.82; MR_α 42.56; MR_β 43.43.

C_9H_{16} F . Calculated: MR_D 41.76; MR_α 41.51; MR_β 42.28.

0.3355 g substance; 22.89 g benzene: Δt 0.62°.

Found: M 120.56

C_9H_{16}. Calculated: M 124.00.

0.0878 g substance: 0.2794 g CO_2; 0.0998 g H_2O.

0.1012 g substance: 0.3225 g CO_2; 0.1151 g H_2O.

Found %: C 86.78, 86.91; H 12.71, 12.74.

C_9H_{16}. Calculated %: C 87.09; H 12.90.

The hydrocarbon does not exhibit the reaction for free acetylenic hydrogen, nor does it react with maleic anhydride; it is colored orange by tetranitromethane. The hydrocarbon yield was 40% of the theoretical.

To determine its structure, 10 g of the hydrocarbon was oxidized with a

chilled alkaline solution of $KMnO_4$. 30 g of the oxidant was used on the assumption that we were dealing with a mixture of acetylenic and allene hydrocarbons (a triple bond would have required 25.5 g, whereas 2 double bonds would have required 34 g of $KMnO_4$). Oxidation was rapid. After the calculated quantity of oxidant had been added, oxidation was stopped, and the MnO_2 precipitate was filtered out. The solution, which exhibited an alkaline reaction, was boiled to drive off the neutral oxidation products, which were collected in a receiver containing a solution of p-nitrophenylhydrazine. p-Nitrophenylhydrazone was precipitated, m.p 123° after recrystallization from methanol, and exhibited no depression when mixed with the p-nitrophenylhydrazone of methyl ethyl ketone.

0.0765 g substance: 13 ml N_2 (18.5°, 772 mm).
Found %: N 20.29.
$C_{10}H_{13}O_2N_3$. Calculated %: N 20.29.

The solution remaining after the neutral products had been driven off was acidulated with sulfuric acid, the volatile acids being driven off with steam. Five fractions, each weighing 15 g, were collected. The first fraction differed from the others in that it constituted an emulsion that was hard to separate into layers. The solutions of acids obtained were heated with freshly prepared silver carbonate over a boiling water bath for 4 hours. The first fraction yielded a silver salt whose composition agreed with that of a salt of methyldiethylacetic acid:

0.0901 g substance: 0.0413 g Ag.
Found %: Ag 45.83.
$C_7H_{13}O_2Ag$. Calculated %: Ag 45.54.

The salts prepared from the other acid fractions yielded the following results:

0.0651 g substance: 0.0415 g Ag.
0.1617 g substance: 0.1036 g Ag.
0.1183 g substance: 0.0760 g Ag.
0.2132 g substance: 0.1375 g Ag.
Found %: Ag 63.74; 64.06; 64.24; 64.49.
$C_2H_3O_2Ag$. Calculated %: Ag 64.67.

2. Reaction of 3-Chloro-3-methylhexyne-4 With C_6H_5MgBr

32.5 g (0.25 mole) of 3-chloro-3-methylhexyne-4 (I) was added drop by drop, with constant stirring, to an organomagnesium compound prepared in the usual manner from 8 g of Mg and 50 g of C_6H_5Br and separated from the residue of unreacted magnesium by decantation. The ensuing reaction liberated heat, but not as intensely as in the reaction with C_2H_5MgBr. The reaction was completed by heating the mixture to 40°for 4 hours, with constant stirring. The reaction product was decomposed with ice water and then with dilute hydrochloric acid. The ether solution was desiccated. The ether was then driven off. The residual liquid was then distilled at reduced pressure. At first, approximately 4 g of a product was distilled; it had a b.p. of 107-108° when distilled at standard pressure and consisted of a hydrocarbon formed by the detaching of HCl from the initial chloride [4]. The bulk of the product was distilled at 92-98° at 7 mm. The hydrocarbon had the following constants after double distillation over metallic sodium:

B.p. 94-95° at 7 mm; d_4^0 0.9402; d_4^{20} 0.9238; n_D^{20} 1.54359; n_α^{20} 1.53813; n_β^{20} 1.55780

Found: MR_D 58.74; MR_α 58.25; MR_β 60.01.
$C_{13}H_{18}F_5$. Calculated: MR_D 57.69; MR_α 57.27; MR_β 58.65.

0.2332 g substance; 21.4 g benzene: Δt 0.315°.
0.1683 g substance; 20.3 g benzene: Δt 0.255°.
Found: M 176.4, 165.5.
$C_{13}H_{16}$. Calculated: M 172.0.
0.0804 g substance: 0.2665 g CO_2; 0.0668 g H_2O.
0.0710 g substance: 0.2352 g CO_2; 0.0586 g H_2O.
Found %: C 90.41, 90.34; H 9.29, 9.23.
$C_{13}H_{16}$. Calculated %: C 90.69; H 9.30.

The hydrocarbon does not react with maleic anhydride, and it is colored orange by tetranitromethane. The hydrocarbon yield was 38% of the theoretical.

The hydrocarbon was oxidized and ozonized to determine its structure.

Oxidation. 5 g of the hydrocarbon was oxidized with a chilled 1% alkaline solution of $KMnO_4$. We used 12.2 g of oxidant on the assumption that two double bonds were present. Oxidation was very rapid, and the characteristic odor of acetophenone was present. After oxidation was complete, the precipitate of manganese dioxide was filtered out, and the neutral products were driven out of the remaining alkaline solution. The first 15 drops were collected in a solution of semicarbazide acetate; then the receiver was changed, and distillation was continued until no more emulsion passed over with the sharp odor of acetophenone. The heavy salt that collected at the bottom of the receiver was separated, dried, and redistilled. This yielded 2 g of acetophenone, with a b.p. of 199-200°.

A small precipitate settled out of the semicarbazide solution; it fused at 198° after recrystallization and exhibited no depression when fused with a standard sample of acetophenone semicarbazone.

After the semicarbazone had been removed, the semicarbazide mother liquor was acidulated with dilute sulfuric acid and then distilled. The distillate was collected in an acetic-acid solution of p-nitrophenylhydrazine. A yellow precipitate was thrown down, which fused at 123° after recrystallization from methanol and exhibited no depression when fused with the p-nitrophenylhydrazone of methyl ethyl ketone.

0.0836 g substance: 15 ml N_2 (25°, 762.6 mm).
0.0620 g substance: 11 ml N_2 (25°, 762.6 mm).
Found %: N 20.23, 20.01.
$C_{10}H_{13}O_2N_3$. Calculated %: N 20.29.

The solution that remained after the neutral products had been eliminated was acidulated with dilute sulfuric acid. A small quantity of precipitate settled out; after sublimation, it fused at 121° and exhibited no depression when fused with benzoic acid.

Ozonation. 4 g of the hydrocarbon was ozonized in deeply chilled solution of chloroform. The chloroform was driven off in vacuum, and the ozonide was decomposed in the presence of chalk. Then the neutral products were distilled off by the method described above under the oxidation of the hydrocarbon. This yielded methyl ethyl ketone, identified as the p-nitrophenylhydrazone, and acetophenone, which was identified by its boiling point and by the preparation of the semicarbazone, which exhibited no depression when fused with a known sample of acetophenone semicarbazone.

Practically no acids were found in the ozonation products, neither in the free state nor as silver salts.

V. I. Lukina participated in this research, and I desire to express my

sincere gratitude to her.

SUMMARY

1. The reactions between a tertiary acetylenic chloride-3-chloro-3-methylhexyne-4 (I) and organomagnesium compounds have been investigated.

2. It has been shown that the reaction of the chloride (I) with C_2H_5MgBr is accompanied by an intramolecular rearrangement, which results in the synthesis of two hydrocarbons: 3,5-dimethylheptadiene -3,4 (II) and 3-methyl-3-ethylhexyne-4 (III).

3. Only an anomalous product, 3-methyl-5-phenylhexadiene -3,4 (IV), is formed when the chloride (I) is reacted with C_6H_5MgBr.

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Received March 7, 1948.

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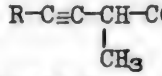
*See CB translation p. 75 ff.

RESEARCH ON THE ISOMERIC TRANSFORMATIONS OF KETONES AND ALDEHYDES OF THE ACETYLENE SERIES. III

F. Y. Perveyev

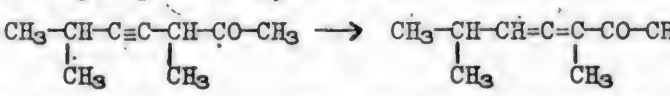
Chair of the Structure of Organic Compounds. Faculty of Chemistry of the A. A. Zhdanov State University of Leningrad, awarded the Order of Lenin.

In our second report we pointed out [1] that the isomerization and the state of equilibrium of the prototropic systems:



depend upon both the radicals R — substituents for the acetylenic hydrogen, and the radicals R' — attached directly to the carbonyl groups.

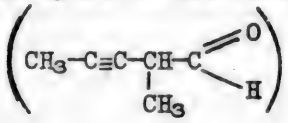
We established the fact that 2,5-dimethylheptyn-3-one-6 is converted into 2,5-dimethylheptadien-3,4-one-6:



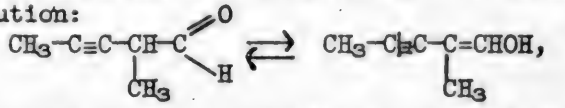
under the synthesis conditions, whereas 1-phenyl-3-methylpentyn-1-one [2] exists as a tautometric mixture:

where the equilibrium is shifted toward the ketone.

Continuing our research into the influence of the radicals that replace the acetylenic hydrogen upon the nature of the isomerization of ketones and aldehydes of the acetylene series, we discovered that 2-methylpentyn-3-al

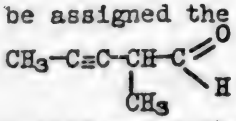


exists as a tautomeric mixture, both in melts and in solution:

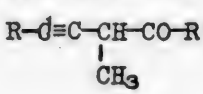


only the enol form being retained in the crystalline state. 4-Methylpentyn-2-en-4-ol-5 consists of colorless crystals that fuse at 33-34°. They quickly turn to liquid when left standing in air, but suffer no change at all when kept in sealed vessels for several months. When mixed with ferric chloride in alcoholic solution, the synthesized substance is colored dark purple; it forms a silver mirror when gently heated with ammoniacal silver nitrate; it reacts with semicarbazide; it reacts vigorously with phenyl isocyanate, forming the respective derivative; and it is titrated with sodium methylate. Both in a melt and in solution (in ether and in methanol) the percentage of the enol form is 60-61%. The structure of the substance was proved by its oxidation with permanganate at 0°. The oxidation products included acetic and proponic acids, which were identified in their silver salts.

Thus this substance may be assigned the following structure:



The presence of propionic acid among the oxidation products of 2-methylpentyn-3-al can apparently be explained as due to decarboxylation of the methylmalonic acid formed during the reaction.

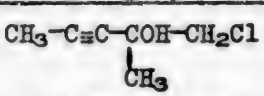
Our results enable us to assert that primary alkyl radicals—substituents for the acetylenic hydrogen in the prototropic systems  stabilize the anolic forms.

The degree of influence of various alkyl radicals upon enolization will depend, not on the length of the chain, but on the number of hydrogen atoms attached to a multiple bond in the hydrocarbon, i.e., their effect in enolization will be the converse of their inductive effect:

$$CH_3 \longrightarrow CH_3{-}CH_2 \longrightarrow (CH_3)_2CH.$$

EXPERIMENTAL

Synthesis of 4-Methyl-5-chloropentyn-2-ol-4



23g of magnesium (chips) and 300 ml of absolute ether were placed in a 1-liter flask, attached to a condenser inverted downward and fitted with a mechanical stirrer and a dropping funnel. 100 ml of ethyl bromide is gradually added from the dropping funnel, with constant stirring and chilling. After all the magnesium in the reaction mixture has been consumed, dry methylacetylene is passed through the flask for 35 hours at room temperature. Then the reaction mixture was heated to 30-34° for 1 hour over a water bath. 90 g of chloroacetone was added to the chilled (water and ice) organomagnesium compound thus produced. After the passage of 12 hours, the organomagnesium coordination compound was decomposed with 10% acetic acid. The reaction product was extracted with ether. The ether solution was washed with water and dried over magnesium sulfate. The synthesized chlorohydrin was distilled in vacuum after the ether had been driven off. The 4-methyl-5-chloropentyn-2-ol-3 boiled at 65-66° and 14 mm after double distillation. It is a colorless, very mobile liquid that darkens upon standing, hydrogen chloride being liberated. The yield was 68-70%, based on the chloroacetone used.

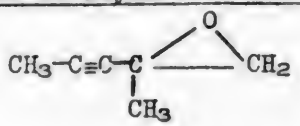
d_4^0 1.1007; d_4^{10} 1.0930; n_α^{10} 1.47494; n_β^{10} 1.48096; MR_α 34.1; MR_β 34.7
C_6H_9COCl F. Calculated: MR_α 34.2; MR_β 34.6.

0.1864 g, 0.1451 g substance: 0.1980 g, 0.1554 g AgCl.
Found %: Cl 26.61, 26.53.
C_6H_9OCl. Calculated %: Cl 26.77.

0.1353 g substance: 0.2689 g CO_2; 0.0825 g H_2O.
0.1402 g substance: 0.2801 g CO_2; 0.0865 g H_2O.
Found %: C 54.2, 54.47; H 6.83, 6.94.
C_6H_9OCl. Calculated %: C 54.35; H 6.94.

0.1364 g, 0.1568 g substance: 22.9 ml 26.1 ml CH_4 (10°, 762 mm).
Found %: OH 11.62, 11.43.
C_6H_9OCl. Calculated %: OH 12.80.

Synthesis of the Oxide of Asymmetrical Methylmethylacetylenylethylene



40 g of powdered potassium hydroxide was added in small batches with constant stirring and chilling to 60 g of chlorohydrin, dissolved in 150 ml of absolute ether. Then the reaction mixture was heated for half an hour to 30-35° over a water bath, and water was added to the reaction vessel until all the inorganic substances dissolved. The oxide obtained was leached out with ether, the ether solution was dried with sodium sulfate, the ether was driven off, and the residual brown liquid was distilled in vacuum.

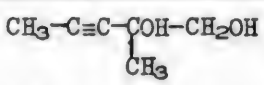
The oxide is a colorless, readily mobile liquid, with a sharp cloying odor and a b.p. of 40-41° at 22 mm. Yield: 70-75%.

d_4^0 0.9392; d_4^{20} 0.9264; n_α^{20} 1.44612; n_β^{20} 1.45324; MR_α 27.7; MR_β 28.0.

C_6H_8O F. Calculated: MR_α 27.6; MR_β 28.1.

0.1413 g substance: 0.3876 g CO_2; 0.1053 g H_2O.
0.1121 g substance: 0.3345 g CO_2; 0.0912 g H_2O.
Found %: C 74.83; 75.21; H 8.53, 8.42.
C_6H_8O F. Calculated %: C 75.00; H 8.34.

Synthesis of the Glycol: 2-Methylpentyne-3-diol-1,2



80 g of water and 2 to 3 drops of hydrochloric acid were placed in a round-bottomed flask. Then 40 g of the oxide was added to the solution in small batches with constant stirring. Considerable heat is evolved in the reaction, so that the reaction flask had to be cooled at intervals with ice. After the reaction was complete, the water was driven off in vacuum, leaving behind a light-brown mass, which was pressed out on a porous dish and then twice recrystallized from benzene. The glycol consists of colorless crystals; m.p. 66-67°.

0.1406 g substance: 0.3264 g CO_2; 0.1121 g H_2O.
0.1204 g substance: 0.2784 g CO_2; 0.0969 g H_2O.
Found %: C 63.05, 63.32; H 8.92, 8.90.
C_6H_8O. Calculated %: C 63.16; H 8.77.

Dehydration of 2-Methylpentyne-3-diol-1,2

50 ml of the glycol, dissolved in 100 ml of water, was added from a dropping funnel to a boiling aqueous solution of oxalic acid. The dehydration product was steam distilled and collected in a chilled receiver. The mobile upper layer formed in the receiver was separated from the aqueous layer and dried with sodium sulfate. The aqueous layer, containing some of the glycol, was returned to the reaction vessel. The reaction was considered to be complete when a sample did not give the characteristic enol color when added to an alcoholic solution of ferric chloride. Then the aqueous layer was repeatedly treated with ether. The ether solution was dried with calcined sodium sulfate, and then the ether was driven off. The residual brown liquid was added to the first fraction.

The synthesized substance was fractionated in vacuum. Double frac-

tionation resulted in the recovery of a fraction that boiled at 45-46° at 10 mm. The liquid recovered crystallized completely in the receiver, the crystals fusing at 33-34°. The yield was 19 g. When the crystals were left exposed to the air, they gradually turned into a liquid at 10-12°, but they remained unchanged for several months when kept in a sealed container.

When treated with an alcoholic solution of ferric chloride, the isolated substance turned dark purple; it formed a silver mirror when gently heated with ammoniacal silver nitrate; and, like acids, it is titrated with sodium methylate.

0.1234 g substance: 0.3387 g CO_2; 0.0925 g H_2O.
0.1345 g substance: 0.3610 g CO_2; 0.1014 g H_2O.
Found %: C 74.86, 74.92; H 8.39, 8.44.
C_8H_8O. Calculated %: C 75.00; H 8.34.

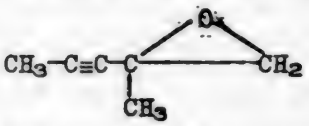
Synthesis of the semicarbazone. Treating the synthesized substance with semicarbazide yields the semicarbazone, which fuses at 122-123°.

0.0888 g, 0.1345 g substance: 21.4 ml, 32.4 ml N_2 (765 mm, 23°).
Found %: N 27.6, 27.53.
$C_7H_{11}ON_3$. Calculated %: N 27.46.

Synthesis of Phenylurethan. 1 g of the substance and 1 g of phenyl isocyanate were placed in a test tube, which was then sealed and set aside overnight. The light-brown crystalline mass that formed was squeezed out on a porous plate and washed a few times with light gasoline. The synthesized phenylurethan fused at 111-112° after double recrystallization from ligroin.

0.1019 g, 0.2509 g substance: 6 ml, 14.5 ml N_2 (769 mm, 24°).
Found %: N 6.71, 6.59.
$C_{13}H_{13}O_2N$. Calculated %: N 6.5.

Isomerization of the Oxide



20 g of the oxide was added to a boiling 15% solution of oxalic acid. The mixture was heated to boiling for 20 minutes with a reflux condenser. Then the isomerization product was steam distilled and collected in a chilled receiver. The steam distillation continued until a qualitative test for enol gave a negative result. The upper mobile layer was separated from the aqueous layer; the aqueous layer was treated with ether; the ether solution was dried with sodium sulfate; and the ether was driven off. The substance recovered was fractionated in vacuum. Double fractionation yielded 9.5 g of a substance that distilled at 45-46° (10 mm). As in the first instance, the liquid, which had a greenish tint, crystallized completely in the receiver. The crystals fused at 33-34°. A test sample mixed with the substance produced by dehydrating the glycol exhibited no depression.

When reacted with semicarbazide, the synthesized substance yielded colorless crystals that fused at 122-123° after double recrystallization from ligroin. The phenylurethan fused at 111-112°.

These figures justify the assertion that the products isolated by dehydrating the glycol and isomerizing the oxide are identical.

The following table gives the data on the percentage of the enol by the method of titration with sodium methylate

I $T_{Na} = 0.001230$

Weight of Substance	Ml of CH_3ONa	Per cent of enol
0.2386	41.2	82.2
0.2463	42.1	87.7
0.2114	36.4	88.4
0.2813	46.3	87.02

II

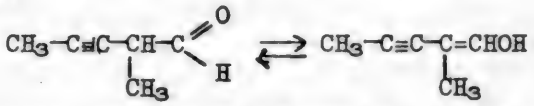
0.2792	32	60.3
0.2085	25.1	61.7
0.2017	24.8	61.6
0.2536	29.5	59.8

III

0.2164	25.9	61.4
0.2376	28.1	60.2
0.2302	27.6	59.8

The figures cited under I are for the case when the crystalline substance was not first placed in solution but was directly titrated with the sodium methylate. The results given under II refer to the batches that were first dissolved in methanol, with titration taking place 40 minutes later. For the third set of figures, titration took place 2 hours after the substance had been placed in solution.

The analytical data indicate that the substance we have synthesized, both by dehydrating the glycol and by isomerizing the oxide, is the enol; it undergoes a change in solution or when exposed to air, forming a tautomeric mixture:



where the percentage of the enol formed is 60-61%.

Oxidation. 6 g of the substance was oxidized with the calculated quantity (33 g) of permanganate at 0°. After oxidation was complete, the MnO_2 was filtered out of the solution.

The manganese dioxide was washed twice with hot water; the wash waters were added to the main solution. After it had been found that no neutral products were present, the solution was evaporated in vacuum and acidulated with sulfuric acid, the volatile acids were driven off with steam, and their silver salts were prepared in the usual manner.

0.1290 g substance: 0.0769 g Ag.
0.1748 g substance: 0.1048 g Ag.
0.1370 g substance: 0.0852 g Ag.
0.1690 g substance: 0.1050 g Ag.
0.2018 g substance: 0.1273 g Ag.
0.2015 g substance: 0.1281 g Ag.
0.1375 g substance: 0.0884 g Ag.
0.1456 g substance: 0.0935 g Ag.
0.1271 g substance: 0.0820 g Ag.
0.1583 g substance: 0.1021 g Ag.

Found %: Ag 59.62, 59.92, 62.25, 62.13, 63.5, 63.53, 64.3, 64.26, 64.53, 64.45.

$C_2H_3O_2Ag$. Calculated%: Ag 64.65
$C_3H_5O_2Ag$. Calculated%: Ag 59.60.

The analytical data indicate that the composition of the silver salts is that of salts of acetic and propionic acids.

SUMMARY

1. 4-Methyl-5-chloropentyn-2-ol-4 was synthesized by condensing methylacetylene with chloroacetone.

2. The action of potassium hydroxide upon 4-methyl-5-chloropentyn-2-ol-4 yielded the corresponding oxide.

3. 2-Methylpentyn-3-al was synthesized by isomerizing the oxide with a 20% solution of oxalic acid and by dehydrating the alpha glycol.

4. Primary alkyl radicals—the substituents of the acetylenic hydrogen in the $R-C\equiv C-\underset{\underset{CH_3}{|}}{CH}-CO-R'$ prototropic systems—stabilize in the enol form.

The degree in which various alkyl radicals affect enolization will depend, not upon the length of the chain, but upon the number of hydrogen atoms attached to carbon at multiple bonds, i.e., their effect upon enolization will vary inversely with their inductive effect.

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[1] F. Y. Perveyev, J. Gen. Chem., 18, 686 (1948).

[2] A. E. Favorsky, J. Gen. Chem., 14, 272 (1944).

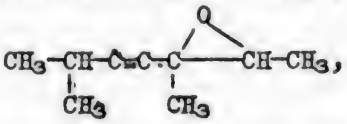
Received April 2, 1948.

RESEARCH IN THE ISOMERIC TRANSFORMATIONS OF KETONES AND ALDEHYDES OF THE ACETYLENE SERIES. IV

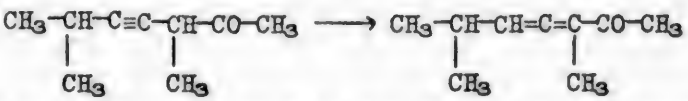
F. Y. Perveyev

Chair of the Structure of Organic Compounds. Faculty of Chemistry of the A. A. Zhdanov State University of Leningrad, awarded the Order of Lenin

It has been established previously [1] that when an oxide of the following structure:

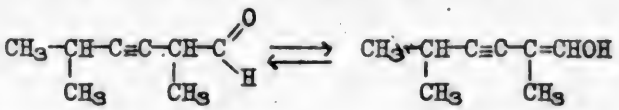


was oxidized by zinc chloride, 2, 5-dimethylheptadien-3,4-one-6 was produced instead of the expected isomeric 2,5-dimethylheptyn-3-one-6, i.e., under these synthesis conditions the following transformation took place:



The 2,5-dimethylheptadien-3,4-one-6 gave no enol reaction with an alcoholic solution of ferric chloride, even when kept in contact with the latter for a long time. Diacetyl and isobutyric acid were found among the products of ozonation of the substance under investigation. This led us to conclude that 2,5-dimethylheptyn-3-one-6 can exist only in its isomeric allene form.

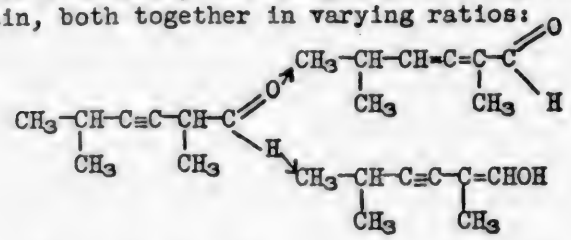
An interesting question for solution is this: is the stability of the allene structure in this type of compound governed by the isopropyl radical, or do the allene rearrangement and the stability of the allene form depend upon other structural features of the molecule ? With this in mind we synthesized 2,5-dimethylhexyn-3-al and studied its properties. We found that the substance synthesized produces a dark purple color with an alcoholic solution of ferric chloride, forms phenylurethan when reacted with phenyl isocyanate, reacts with semicarbazide, and is titrated with sodium methylate, i.e., it behaves like the tautomeric mixture:



The percentage of the enol form in the mixture is 50%. During determination of the enol percentage it was noticed that no further shift of the equilibrium occurred after all the enol form in the mixture had been titrated back. The question arose: are these stable isomers that are formed under the synthesis conditions, or is this a tautomeric mixture ?

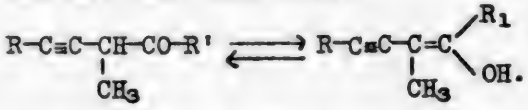
A. E. Favorsky believed [2] that the acetylenic aldehydes produced during the synthesis undergo isomeric transformations at the instant of

their formation, the end products being either allene aldehydes or enols, or again, both together in varying ratios:

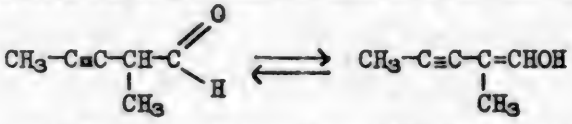


The available facts are in consonance with these assertions. For example, 4-phenyl-2-methylbuyn-3-al [1] is stable only in the enol form; 2,5,5-trimethylhexyn-3-al [4], on the other hand, is stable in the allene form.

In the general case, however, there must be a reciprocal-reversible conversion of the keto and enol forms:



The sole difference between the various compounds of a given class is the velocity of the reciprocal transformation of the isomers; to a lesser degree this difference depends upon the relative percentages of the two forms in a status of equilibrium. We were able to prove experimentally that 2-methylpentyn-3-al exists as a tautomeric mixture in the liquid state and in solution:



where the enol form constitutes 60-61% of the total.

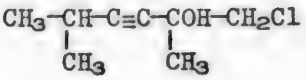
In the crystalline state only one form is present--the enolic. When the liquid tautomeric mixture is set aside to stand in the cold or is distilled, we get colorless crystals that fuse at 33-34°. When the crystalline substance is left standing in the air, it quickly returns to the liquid state, but it suffers no visible change over the course of several months when kept in a sealed vessel.

In addition to this striking example of the reciprocal transformation of isomers, extreme cases are possible as well: in some compounds the velocity of reciprocal conversion is too high for the independent forms to be isolated; in others it is so low that it is impossible to record any reciprocal shifts in ordinary intervals of time without recourse to catalysts and increased temperature; in still other compounds, equilibrium is shifted so far to one side that it is only indirectly that reversibility can be detemined.

As for the allene structure, it may arise during the synthesis and be present in the mixture. But it is hard to see how a labile equilibrium can exist among three isomers under ordinary conditions, since the transition from the allene structure to the acetylenic and enolic structures would be hampered by the fact that in the allene configuration ($R-CH=C=C-COR'$) the hydrogen atom becomes less mobile.

EXPERIMENTAL

Synthesis of 2,5-Dimethyl-6-chlorohexyn-3-ol-5



Ethyl bromide was added drop by drop, with chilling and constant stirring, to 17 g of magnesium chips and 300 ml of absolute ether in a round bottomed flask. After the magnesium had dissolved, 38 g of isopropylacetylene was added in small batches. The termination of the reaction was judged by the amount of ethane evolved. After the hydrocarbon had been added, the temperature of the water bath was raised to 30°. Then 43 g of chloroacetone, dissolved in 20 ml of absolute ether, was added to the reaction mixture. The mixture was set aside to stand overnight.

The dark-red coordination compound produced was carefully decomposed with 20% acetic acid, with constant agitation and chilling. The ethereal layer was removed in a separating funnel and repeatedly washed with water, after which it was dried with sodium sulfate, and the ether was driven off.

The chlorohydrin synthesized boiled at 74-75° and 7 mm after double distillation. It is a mobile, light-yellow liquid with a pleasant odor. It grows dark in storage, even in a sealed vessel. The yield was 79%, based on the isoproylacetylene used in the reactibn.

d_4^0 1.0321; d_4^{13} 1.0200; n_α^{13} 1.46347;

n_β^{13} 1.47455; MR_α 43.4; MR_β 44.3;

$C_8H_{13}OCl$ ⊨. Calculated: MR_α 43.4; MR_β 44.1.

0.1512 g, 0.1364 g substance: 0.1353 g, 0.1223 g AgCl.

Found %: Cl 22.19, 22.24.

$C_8H_{13}OCl$. Calculated %: Cl 22.10

0.1343 g, 0.1474 g substance: 0.2958 g, 0.3241 g CO_2; 0.0972 g, 0.1067 g H_2O

Found %: C 60.08, 59.97; H 8.18, 8.14.

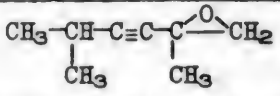
$C_8H_{13}OCl$. Calculated %: C 59.88; H 8.10.

0.1178 g, 0.1360 g substance: 17.8 ml, 20.2 ml CH_4 (13°, 761 mm).

Found %: OH 10.94 10.75.

$C_8H_{13}OCl$. Calculated %: OH 10.4.

Synthesis of the Oxide of Asymmetrical Methylisopropylacetylenylethylene



120 g of powdered potassium hydroxide was added in small batches, with constant agitation and chilling, to 60 g of the chlorohydrin, dissolved in 200 ml of absolute ether. Then water was added to the flask – chilled with ice water – until all the inorganic substances had dissolved. The ether solution was removed, washed with water, and dried with sodium sulfate.

The synthesized oxide was a highly mobile greenish liquid with an acrid odor. Its b.p. was 45-46° at 9 mm. The yield was 80-85%.

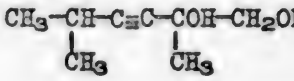
d_4^0 0.8911; d_4^{11} 0.8815; n_α^{11} 1.44243;

n_β^{11} 1.45176; MR_α 37.2; MR_β 37.9.

$C_8H_{12}O$ ⊨. Calculated: MR_α 36.9; MR_β 37.7.

0.1093 g substance: 0.3399 g CO_2; 0.0945 g H_2O.
0.1234 g substance: 0.3505 g CO_2; 0.1078 g H_2O.
Found %: C 77.32, 77.50; H 9.77, 9.85.
$C_8H_{12}O$. Calculated %: C 77.42; H 9.67.

Synthesis of the Glycol 2,5-Dimethylhexyne-3-Diol-1,2

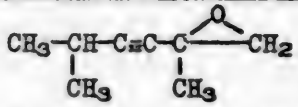


When the oxide is treated with water in the presence of traces of hydrochloric acid, the glycol is formed. The reaction of adding water is fairly rapid, with considerable heat being liberated. The glycol consists of colorless crystals, which fuse at 58-59° after double recrystallization from 40% methanol

0.1306 g substance: 0.3245 g CO_2; 0.1149 g H_2O.
0.1433 g substance: 0.3550 g CO_2; 0.1265 g H_2O.
Found %: C 67.51, 67.76; H 9.74, 9.82.
$C_8H_{14}O_2$. Calculated %: C 67.60; H 9.80.

0.0937 g, 0.1063 g substance: 29 ml, 33.7 ml CH_4 (14°, 761 mm).
Found %: OH 20.2, 22.4.
$C_8H_{14}O_2$. Calculated %: OH 21.18.

Isomerization of the Oxide



40 g of the oxide was added in small batches to a boiling 5% solution of oxalic acid. The isomerization product was steam distilled and collected in a chilled receiver, after which it was extracted with ether, dried with potash, and distilled in vacuum. B.p. 68-69° at 12 mm. The substance recovered had an acrid odor. In a gaseous state it irritates the skin and the eyes. Considerable tarring takes place during distillation. The yield was 46-50%.

d_4^0 0.9134; d_4^{17} 0.8943; n_α^{17} 1.4668;
n_β^{17} 1.4834; MR_α 38.1; MR_β 38.9.
$C_9H_{12}O$ F. Calculated: MR_α 38.1; MR_β 39.5 (for the enol); MR_α 36.9; MR_β 37.6 (for the ketone).

0.1082 g, 0.1173 g substance: 0.3068 g, 0.3322 g CO_2; 0.0938 g, 0.1017 g H_2O.
Found %: C 77.38, 77.2; H 9.7, 9.8.
$C_8H_{12}O$. Calculated %: C 77.42; H 9.67.

0.1356 g, 0.1771 g substance: 16.4 ml, 18.2 ml CH_4 (15°, 762).
Found %: OH 8.7, 8.8.
$C_8H_{12}O$. Calculated %: OH 13.7.

0.1921 g substance; 21.42 g of benzene: Δt 0.38°.
0.1423 g substance; 21.42 g of benzene: Δt 0.28°.
Found: M 120.1, 121.3.
$C_8H_{12}O$. Calculated: M 124.

When the synthesized substance is reacted with ferric chloride in an alcoholic solution, it produces an intense purple color; it is titrated with sodium methylate, and it forms derivatives of both the ketonic and the enolic forms.

Synthesis of phenylurethan. 0.5 g of the substance and 0.8 g of phenyl isocyanate were placed in a test tube, which was then sealed and heated over a water bath for 15 minutes, after which it was set aside for 8 hours. The light-yellow mass that formed was squeezed out on a porous plate and washed with ligroin. The phenylurethan fused at 97.98° after double recrystallization from ligroin.

0.1137 g, 0.1246 g substance: 5.8 ml, 6.2 ml N_2 (15°, 757 mm)

Found %: N 5.96, 5.8.

$C_{15}H_{17}O_2N$. Calculated %: N 5.7

The substance under analysis yielded a semicarbazone when reacted with semicarbazide. The crystals of the semicarbazone fused at 132-133° after being twice recrystallized from 50% methanol.

Determination of the enol by titration with sodium methylate. (T_{Na} = 0.00124), yielded the following results:

0.1322 g substance: 9.9 ml CH_3ONa.
0.1087 g substance: 8.8 ml CH_3ONa.
0.1123 g substance: 8.8 ml CH_3ONa.
0.1224 g substance: 9.7 ml CH_3ONa.

Found %: of enol 50.6, 53.3, 52.6, 52.9.

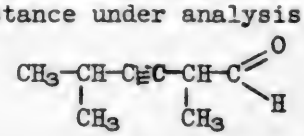
Oxidation. 5 g of the substance under analysis was oxidized with the calculated amount of permanganate at 0°. After oxidation, the MnO_2 was filtered out of the solution. The manganese dioxide was twice washed with hot water, the wash waters being added to the original solution. As soon as it was found that no neutral products were present, the solution was evaporated in vacuum and acidulated with sulfuric acid; the volatile acids were driven off with steam, and their silver salts were prepared.

0.1356 g substance: 0.0775 g Ag.
0.1368 g substance: 0.0786 g Ag.
0.1475 g substance: 0.0876 g Ag.
0.1246 g substance: 0.0759 g Ag.
0.1137 g substance: 0.0728 g Ag.
0.1089 g substance: 0.0697 g Ag.
0.1184 g substance: 0.0759 g Ag.

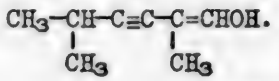
Found %: Ag 55.9, 57.3, 59.4, 62.4, 64.1, 64.3, 64.2.

The analytical data make it seem likely that the silver salts are salts of isobutyric and acetic acids. It is not impossible that a salt of propionic acid is also present in the mixture. The silver acetate contains 64.65% of silver, the propionate 59.64%, and the isobutyrate 55.38%.

On the basis of our analytical results we may ascribe the following structure to the substance under analysis:



Acetic acid is apparently formed as the result of the decomposition of pyruvic acid, which is formed during the oxidation of the enol form:



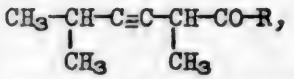
SUMMARY

1. 2,5-Dimethyl-6-chlorohexyn-3-ol-5 has been synthesized by condensing isopropylacetylene with chloroacetone.

2. Reacting powdered potassium hydroxide with 2,5-dimethyl-6-chlorohexyn-3-ol-5 yields the corresponding oxide.

3. Isomerization of the oxide with a 20% solution of oxalic acid yields 2,5-dimethylhexyn-3-al, which is a tautomeric mixture:

4. Secondary alkyl radicals—substituents for the acetylenic hydrogen—bring about an allene rearrangement in acetylenic ketones of the following class:



whereas they stabilize the enol forms, like the primary radicals, in acetylenic aldehydes.

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[2] A. E. Favorsky, J. Gen. Chem., 14, 75 (1944).

[3] A. E. Favorsky and Tikhomolov, J. Gen. Chem., 10, 1501 (1940).

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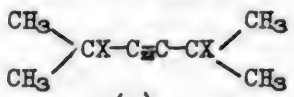
THE ACTION OF CONCENTRATED HYDROCHLORIC ACID UPON DIACETYLENIC GLYCOLS

I. M. Gverdtsiteli and G. V. Tskhadadze, student

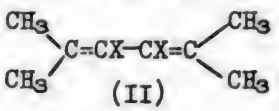
Organic Chemistry laboratory of the J. V. Stalin State University of Tbilisi

Little work has been done upon the action of hydrohalic acids upon γ-acetylenic glycols. By reacting hydrobromic acid and tetramethylbutynediol, Dupont [1] synthesized a crystalline dibromide with a m.p. of 39°, to which he ascribed the structure (I), where X = Br:



(I)

As for the product of the reaction between tetramethylbutynediol and hydrochloric acid, the only data given are the melting point and boiling point of the dichloride produced. Y. S. Zalkind and his co-workers [2] likewise explored the action of HBr on tetramethylbutynediol. The authors assert that the dibromide synthesized by Dupont has the structure (II), where X = Br:



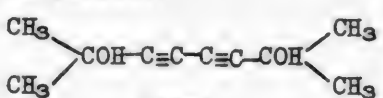
(II)

Dupont produced two dibromides by reacting phosphorus tribromide with tetramethylbutynediol. V. N. Krestinsky [3] succeeded in producing three dibromides—two crystalline and one liquid—by reacting phosphorus tribromide with this glycol.

A. I. Zakharova and her student, I. M. Stroiman [4] explored the action of concentrated hydrochloric acid upon tetramethylbutynediol in great detail. They succeeded in isolating and identifying two dichlorides, with b.p. of 65-67° and 80-82° at 15 mm.

All the above authors mention the inertness of the products synthesized (the dibromides and dichlorides). A. I. Zakharova and I. M. Stroiman were unable to fix the structure of the dichlorides precisely, owing to their inertness. The authors attributed Structure (II), with X=Cl, to the first product, with the b.p. of 65-67°, and Structure (I), with X=Cl, to the second product, with the b.p. of 80-82°.

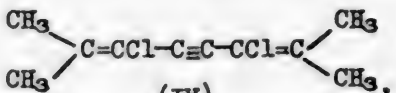
We were interested in checking the action of concentrated hydrohalic acids upon diacetylenic glycols. We selected 2,7-dimethyloctadiyne-3,5-diol-2,7 (III) for this purpose:



(III)

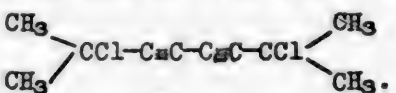
Several experiments showed that the action of concentrated hydrochloric acid produces two isomeric dichlorides: one, a liquid with a b.p. of 64-67° at 4 mm, and the other, crystals with a m.p. of 59.5-60°. The liquid dichloride polymerizes rapidly upon standing, being converted into a solid black polymer with in two to three weeks. The crystalline dichloride is more stable, merely turning yellow during the passage of 12 months.

Both of these dichlorides proved to resist saponification; the initial substance was recovered unchanged even after two days' heating with 15% potash. We assigned the hypothetical structure (IV) to the dichloride with a b.p. of 64-67° at 4 mm:



(IV)

and structure (V) to the dichloride with a m.p. of 59.5-60°:



(V)

EXPERIMENTAL

5 g of the glycol (III) was placed in a 250-ml flask fitted with a reflux condenser, and 45 ml of hydrochloric acid (d_{20}^{20} 1.15) was added. The reaction mixture was heated to 60-70° for one hour over a water bath, being stirred at intervals. Two layers were formed: the dark top layer was removed, washed with water and then with a weak solution of $NaHCO_3$, and dissolved in ether. The ether solution was dried with calcium chloride. After the ether had been driven off, the substances was distilled in vacuum (total yield of crude product: 45%). The following fractions were collected:

Fraction I: b.p. 64-67° at 4 mm
Fraction II: b.p. 67-74° at 4 mm
Fraction III: b.p. 74° at 4 mm

Fraction III crystallized upon standing. It yielded white crystals with a m.p. of 59.5-60°

Analysis of the substance with a b.p. of 64-67° at 4 mm. This substance is a colorless liquid with a pleasant odor (it turns greenish when exposed to light):

d_{20}^{20} 0.993; n_D^{20} 1.5477.

0.1698 g substance; 20.334 g of benzene: Δt 0.202°.
0.2050 g substance; 18.98 g of benzene: Δt 0.282°.
Found: M 206.7, 195.23.
$C_{10}H_{12}Cl_2$. Calculated: M 203.

0.200 g substance: 19.65 ml 0.1 N $AgNO_3$.
Found %: Cl 34.37.
$C_{10}H_{12}Cl_2$. Calculated %: Cl 34.95.

No methane was liberated during the Tserevitinoff determination of active hydrogen.

Analysis of the substance with a m.p. of 59.5-60°.

0.026 g substance; 0.266 g of camphor: Δt 18°.
Found: M 217.
$C_{10}H_{12}Cl_2$. Calculated: M 210.

0.100 g substance: 9.62 ml 0.1 N $AgNO_3$.
Found %: Cl 34.14.
$C_{10}H_{12}Cl_2$. Calculated %: Cl 34.95.

SUMMARY

1. The reaction between 2,7-dimethyloctadiyne-3,5-diol-2,7 and concentrated hydrochloric acid has been investigated.

2. Two isomeric dichlorides, with the molecular formula $C_{10}H_{12}Cl_2$, have been isolated and identified.

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[2] Y.S.Zalkind and assoc., J. Russ. Phys. Chem. Soc., 58, 1039, 1044, 1052 (1926); Y.S.Zalkind and Kruglyakova, J. Russ. Phys. Chem. Soc., 61, 803 (1929).

[3] V.N.Krestinsky and Bazhenova-Kozlovskaya, J. Russ. Phys. Chem., Soc. 61, 1691 (1929).

[4] A.I.Zhakarova and the student I.M.Stroiman, J. Gen. Chem., 15, 441 (1945).

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ANOMALOUS REACTIONS OF α-BROMOKETONES

III. RESEARCH ON α-BROMO-p-TOLYLACETONE

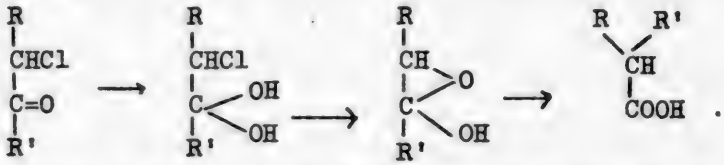
T. I. Temnikova and V. I. Veksler

Chair of the Structure of Organic Compounds. A. A. Zhdanov State University of Leningrad, awarded the Order of Lenin

It is known that α-bromo- and α-chloroketones can enter into various isomeric transformations during reactions in which the halogen is replaced by a hydroxy or alkoxy group or by an ester rearrangement.

After A. E. Favorsky's discovery of the ability of α-ketones to convert into acids when acted upon by caustic alkalis [1], and to partially form α-ketonic alcohols, isomeric with those expected [2], when hydroxyl replaces the chlorine or bromine, considerable research was done on topics in this field.

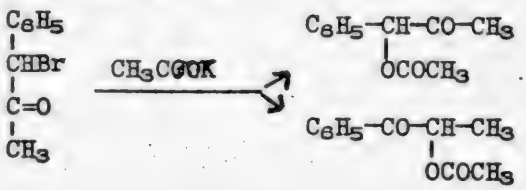
A. E. Favorsky explained the mechanism of the formation of anomalous reaction products by his hypothesis that what first happens is the addition of the reagent to the carbonyl group; then the alkali detaches HCl, and the epoxide, which is unstable and unable to exist independently, undergoes a molecular rearrangement at the instant it is formed [4]:



A. E. Favorsky's diagram, which explains the formation of various anomalous products orginating with bromo- and chloroketones, has now been adopted by all the American researchers working in this field, without citing A. E. Favorsky's research.

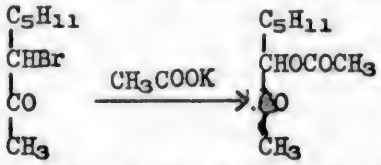
Previously, T. I. Temnikova [3] had shown, by means of the reaction of α-bromobenzyl methyl ketone and α-bromoethyl phenyl ketone with potassium acetate and benzoate, that the direction the reaction takes depends upon the structure of the initial bromoketone as well as upon the reagent employed.

When α-bromoethyl phenyl ketone was used, normal reaction products were obtained with both reagents. When α-bromobenzyl methyl ketone was used, we got, in addition to the normal products, anomalous reaction products: esters corresponding to ethylbenzoylcarbinol; these latter appeared with particular suddenness when potassium acetate was used in the reaction:



A diagram resembling that of A. E. Favorsky's, but slightly modified, was proposed to explain the formation of the acetate of ethylbenzoylcarbinol.

But as our previous reports demonstrated [5], the presence of the carbinol group, which can enter into addition reactions, does not alone determine the possibility of forming anomalous products in substitution reactions of the bromoketones, since only normal products are formed when α-bromohexyl methyl ketone is reacted with potassium acetate:



Thus, the mechanism of the formation of esters of isomeric α-ketonic alcohols has not been elucidated up to the present time. There are no indications whether there is any relationship between the change in the reactivity of the bromine and the relative quantity of the anomalous reaction product formed. Nor is the reason for the rather high reactivity of the halogen in α-halogen carbonyl compounds, as compared with other halogen derivatives, clear.

Backer [6] investigated the influence of a ring substituent upon the velocity constant of the reaction beween pyridine and substituted α-bromoacetophenones and showed that a diminution of the + charge on the carbon atom of the carbonyl group results in a diminution of the constant:

For $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2Br$ + pyridine, $\underline{K} = 0.79 \cdot 10^{-3}$;

For $CH_3C_6H_4-\overset{O}{\overset{\|}{C}}-CH_2Br$ + pyridine, $\underline{K} = 0.74 \cdot 10^{-3}$;

For $NO_2-C_6H_4-CO-CH_2Br$ + pyridine, $\underline{K} = 1.9 \cdot 10^{-3}$.

The present research was undertaken in order to explore still further the isomeric transformations observed when α-bromoketones react with salts of organic acids. As the most typical example is the reaction of α-bromobenzyl methyl ketone with potassium acetate, resulting in the formation of a mixture of esters with the isomeric ones predominating; we were interested in exploring the homologue containing a methyl group at the para position. Introduction of this group produced conditions that facilitated a greater supply of electrons to the reaction zone. The points of interest were:

1) How would this change the reactivity of the bromine toward the CH_3COOK, compared to that of the α-bromobenzyl methyl ketone that was unsubstituted at the phenyl group?

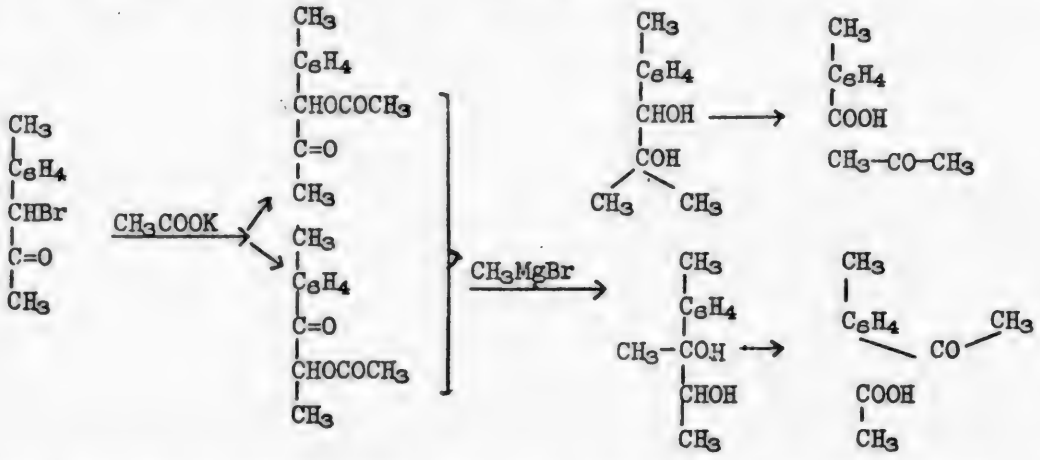
2) How would a change in the reactivity of the bromine affect the yield of the anomalous reaction product, the isomeric ester, when the bromoketone was reacted with potassium acetate?

The p-tolylacetone required for the reaction was formerly produced in various ways from rather inaccessible materials and with extremely low yields. We synthesized it from toluenemagnesium bromide and chloroacetone, like the synthesis of phenylacetone [7]:

$$CH_3C_6H_4MgBr + CH_3COCH_2Cl \longrightarrow CH_3C_6H_4CH_2COCH_3 + MgBrCl.$$

The bromoketone was prepared by the direct bromination of the ketone in a solution of chloroform or of carbon tetrachloride.

The reaction of bromo-p-tolylacetone with potassium acetate is extremely violent: when the bromoketone is added to potassium acetate in ethyl alcohol, intense heat is liberated, the solution boiling up and an abundant precipitate of KBr separating out. The reaction is practically over in a few minutes. The ester, isolated after the usual treatment, was converted into a glycol by methylmagnesium bromide in order to test its homogeneity, and the glycol was then oxidized with lead tetraacetate. The oxidation products comprised a negligible quantity of p-tolyl methyl ketone, a large quantity of p-toluic acid, and acetone. The recovery of p-tolyl methyl ketone is proof that an isomeric ester is present in the mixture, while the recovery of only a negligibly small quantity of the latter (as the semicarbazone) testifies to the fact that the reactions form only a negligible proportion of anomalous product. The foregoing may be expressed by the following diagram:



Thus, increasing the electron density in the zone of the carbon atom to which the bromine atom is attached resulted in a considerable increase in the reactivity of the latter toward potassium acetate, which is manifested in the much more energetic reaction that occurs when the bromoketone and potassium acetate are mixed together, compared to the α-bromo-α-phenylacetone with no ring substitution.* On the other hand, attaching the methyl group to the phenyl ring at the para position very greatly reduced the tendency of the reaction to form an anomalous product, compared to the α-bromophenylacetone. In our experiment, only traces of the ester of methyl-p-tolylcarbinol were obtained, whereas the ester corresponding to methylbenzoylcarbinol was the predominant reaction product in the case of α-bromophenylacetone.

We are continuing our research to determine the structural factors that affect the course of the process in order to establish the mechanism of reactions in which the halogen is replaced in halogen ketones.

EXPERIMENTAL

Synthesis of tolylacetone. A solution of 32 g of chloroacetones in ether was added, with stirring and chilling, to a Grignard reagent, prepared from 86 g of p-bromotoluene (b.p. 180-182°) and 14 g of magnesium. Then the reaction flask was connected to an inverted condenser, and all the ether was driven off over a water bath. Toward the end, when most of the ether had been driven off and the bath temperature had been raised to about 100°, the organomagnesium co-

*(α-bromobenzyl methyl ketone).

ordination compound was seen to swell up, and the contents of the flask solidified as a porous mass. This was decomposed with water, with periodic additions of ether; in the normal reaction no basic salts of magnesium are formed. The ether solution was dried with $CaCl_2$. Fractional distillation yielded 29 g of tolylacetone, with a b.p. of 92-94° at 3 mm, or 111° at 12 mm.

The ketone had a b.p. of 102° at 6 mm after it had been purified with a bisulfite compound:

d_4^0 0.9987; d_4^{19} 0.9831; n_α^{19} 1.50970; n_β^{19} 1.52518.

MR_α 45.01; MR_β 46.21; $MR_\beta - MR_\alpha$ 1.20.

$C_{10}H_{12}O$ F_3. Calculated: MR_α 44.48; MR_β 45.48; $MR_\beta - MR_\alpha$ 1.00

Subsequent experiments indicated that tolylacetone is recovered directly from the synthesis in adequate purity, possessing the same refractive index.

The semicarbazone of the ketone had a m.p. of 155-156° (the figure given in the literature is 158°. [8]).

0.1001 g substance: 18.00 ml N_2 (22.5°, 763.5 mm).

Found %: N 20.85.

$C_{11}H_{15}O$ F_3. Calculated%: N 20.47.

The oxime had a m.p. of 88-89° (the figure given in the literature is 90-91° [8].

Oxidation of the ketone. 3 g of the ketone was added to an alkali bromide, prepared with 6.6 g of NaOH, 9.6 g of bromine, and 56 ml of water and the flask contents were set aside to stand overnight. The oil (bromoform) that formed was separated. The aqueous layer was evaporated in vacuum; the crystalline acid that precipitated out when the mixture was acidulated with sulfuric acid was recrystallized from water; m.p. 179-180°, which corresponds to p-toluic acid.

Synthesis of α-bromo-p-tolylacetone. 30 g of bromine in 100 ml of $CHCl_3$ was added to 30 g of the ketone in 75 ml of $CHCl_3$, with stirring and chilling. The reaction set in at once. The chloroform was driven off after the reaction mixture had been washed with water and soda and dried with $CaCl_2$, and the residue was distilled in vacuum.

Two fractional distillations yielded a slightly yellowish substance with a b.p. of 127-128° at 4 mm; the yield was 28%:

d_4^{17} 1.3562; n_α^{17} 1.55448; n_β^{17} 1.57362.

MR_α 53.71; MR_β 55.23; $MR_\beta - MR_\alpha$ 1.52.

$C_{10}H_{11}OBr$ F_3. Calculated: MR_α 52.19; MR_β 53.37; $MR_\beta - MR_\alpha$ 1.18.

0.1937 g substance: 0.1594 g AgBr.

0.1857 g substance: 0.1488 g AgBr.

Found %: Br 35.02, 34.89.

$C_{10}H_{11}OBr$. Calculated %: Br 35.20.

Oxidation of the bromoketone with potassium permanganate in an alkaline medium yielded a substance with a m.p. of 180-181°; a test sample mixed with p-toluic acid had the same melting point. The aqueous solution, which contained no p-toluic acid, was treated with $AgNO_3$; the AgBr recovered was 93% of the theoretical.

Reaction of bromo-p-tolylacetone with potassium acetate. 28 g of bromotolylacetone was added to a warm solution of 16 g of CH_3COOK in 100 ml of absolute ethyl alcohol; KBr was thrown down at once, the solution heating up intensely and sometimes boiling. After 10 minutes a Beilstein test for halogen in the solution was negative. The precipitate was separated out, and the alcohol driven off over a water bath. The oil that separated when water was added was extracted with ether, and the ether solution dried with Na_2SO_4; after the ether had been driven off, the residue was distilled in vacuum. Fractionation yielded a substance that was odorless and almost colorless and distilled at 139-140° at 5 mm. The yield was 17 g:

d_4^0 1.106; n_α^{17} 1.50491; n_β^{17} 1.51981.

$MR\alpha$ 56.26; MR_β 57.65; $MR_\beta - MR_\alpha$ 1.39.

$C_{12}H_{14}O_3$ =3. Calculated: MR_α 55.21; MR_β 56.38; $MR_\beta - MR_\alpha$ 1.27.

0.1428 g substance: 0.3648 g CO_2; 0.0877 g H_2O.
0.1418 g substance: 0.3610 g CO_2; 0.0843 g H_2O.
Found %: C 69.71, 69.43; H 6.87, 6.65.
$C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

The acetate, which boiled over a wider range, 138-141° at 4 mm, was prepared in a similar manner. Analysis of this latter product likewise yielded satisfactory results.

0.1095 g substance: 0.2795 g CO_2; 0.0700 g H_2O.
0.1303 g substance: 0.3350 g CO_2; 0.0817 g H_2O.
Found %: C 69.66, 70.16; H 7.15, 7.02.
$C_{12}H_{14}O_3$. Calculated %: C 69.89; H 6.84.

Reaction of CH_3MgBr with the acetate. An ethereal solution of 6.5 g of the acetate with a b.p. of 138-141° at 4 mm, was added with ice-chilling to a Grignard reagent, prepared from 6 g of magnesium and gaseous CH_3Br in anhydrous ether. It was allowed to stand overnight, and the next day the flask's contents were heated for 5 hours until the ether gently boiled. After the customary disintegration, drying of the ether solution with Na_2SO_4, and driving off of the ether, the residue was fractionated. The trimethylcarbinol was drawn off by a vacuum pump and was not collected. The following fractions were obtained:

Fraction I: up to 148° at 7 mm. . . 0.7 g
Fraction II: 148–151° at 7 mm. . . . 3.6 g

The latter fraction, which was a thick, viscous liquid, crystallized completely after a few days had elapsed. After Fraction I had been seeded, it crystallized as well. The crystals of the principal fraction did not have a sharp melting point; they grew noticeably softer at 32° and melted finally at 45°. Fraction II was analyzed.

0.1144 g substance: 0.3087 g CO_2; 0.0936 g H_2O.
Found %: C 73.64; H 9.15.
$C_{11}H_{16}O_2$. Calculated %: C 73.30; H 8.94.

Recrystallization from light gasoline yielded almost pure 1-tolyl-2-methylpropandiol-1,2, with a m.p. of 53.5-55°.

Oxidation of the glycol with m.p. of 32-45°. 6.5 g of lead tetraacetate was added to 2.5 g of the glycol, dissolved in 20 ml of acetic acid. Mixing these components produced a violent reaction. After being allowed to stand

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*According to the literature [9], the glycol n-$CH_3C_6H_4$- CHOH - $COH(CH_3)_2$ melts at 56-57.5° and boils at 168° at 14 mm.

for half an hour, the mixture was heated with a reflux condenser to 40°. Then the acetic acid was neutralized with a potash solution; the light volatile oxidation products, which were extracted with a current of CO_2, were collected in a solution of p-nitrophenylhydrazine acetate.

A yellow precipitate soon began to settle out; it melted at 142° after recrystallization from alcohol, and a test sample mixed with the known p-nitrophenylhydrazone of acetone exhibited no depression.

After neutralization of the acetic acid, water was added to the flask, and the neutral oxidization products were driven off. The distillate, consisting of an emulsion with a large amount of oil, gave a positive reaction for aldehydes, and it therefore was oxidized with ammoniacal silver nitrate until the aldehyde reaction was negative. Then the neutral products were again driven off, only a negligible quantity of emulsion being recovered. After ether extraction and driving the ether off, the residue was treated with a semicarbazide solution. The resulting semicarbazone (0.19 g), recrystallized from methanol, had a m.p. of 192-194°. A test sample, mixed with the semicarbazone of p-tolyl methyl ketone, which fuses at 198.5-200.5°, fused at 196-198°.

0.0625 g substance: 12.1 ml N_2 (18°, 754 mm).
Found %: N 22.34.
$C_{10}H_{13}ON_3$. Calculated %: N 21.98.

It is noteworthy that the semicarbazone of the p-tolyl methyl ketone synthesized by oxidizing the glycol differs from the semicarbazone of the synthetic p-tolyl methyl ketone in that it turns slightly green at the surface when exposed to light; the green coloring disappears when it is heated to 125°.

The alkaline solutions of the neutral product distillate were acidulated, and an acid (0.95 g), with a m.p. of 174-175°, corresponding to p-toluic acid, was recovered by steam distillation.

SUMMARY

1. It has been shown that the reaction of α-bromo-p-tolylacetone with potassium acetate yields principally the normal reaction product: the acetate of p-tolylacetylcarbinol, the reaction being accompanied by only a negligible amount of molecular rearrangement resulting in an isomeric ester, corresponding to methyl-p-tolylcarbinol.

2. Comparison of the results of this research with those of the investigation into the reaction between α-bromophenylacetone and potassium acetate indicates that increasing the electron density in the reaction zone results in a pronounced increase in the reactivity of the bromine in the reaction with potassium acetate and in a great decrease in the quantity of anomalous reaction product recovered.

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RESEARCH ON ISOMERIC TRANSFORMATIONS OF ALPHA KETONIC ALCOHOLS

VII. THE EFFECT OF CHLORINE IN THE PARA POSITION UPON THE STABILITY OF ALIPHATIC - AROMATIC α - KETONIC ALCOHOLS.: METHYL-p-CHLOROBENZOYLCARBINOL

T. I. Temnikova anf E. I. Kulachkova

Chair of the Structure of Organic Compounds: A. A. Zhdanov State University of Leningrad, awarded the Order of Lenin

Research in the field of the isomeric transformations of alpha ketonic alcohols goes back to the investigations of A. E. Favorsky and his co-workers. They established the fact [1] that transformations of the alpha ketonic alcohols of the aliphatic series are effected so as to form isomers, containing a C=O group close to the end of the carbon chain; alpha ketonic alcohols containing the acetyl group:

$$R{-}CO{-}CHOH{-}CH_3 \longrightarrow R{-}CHOH{-}CO{-}CH_3.$$

are marked by very high stability.

A similar type of isomeric transformation was predicted by A. E. Favorsky for the aliphatic-aromatic alpha ketonic alcohols as well; of the two isomers - methylbenzoylcarbinol and phenylacetylcarbinol, the latter ought to be the more stable one:

$$C_6H_5{-}CO{-}CHOH{-}CH_3 \longrightarrow C_6H_5{-}CHOH{-}CO{-}CH_3.$$

This hypothesis was subsequently proved experimentally [3].

To many, this trend of isomeric transformation seemed incomprehensible, since the presence of conjugation between the phenol and carbonyl groups ought to have, it seemed, ensured greater stability for the ketonic alcohol with the benzoyl grouping [4].

The next pair of isomeric aliphatic-aromatic alpha ketonic alcohols was investigated by T. I. Temnikova and E. F. Afanasyeva [5]; both of these ketonic alcohols, ethylbenzoylcarbinol and phenylpropionylcarbinol, proved to be approximately equally stable. Under the conditions that facilitated their reciprocal conversion, equilibrium was established with a slight preponderance of the ketonic alcohol containing the benzoyl grouping:

$$C_6H_5{-}CO{-}CHOH{-}C_2H_5 \rightleftarrows C_6H_5{-}CHOH{-}CO{-}C_2H_5.$$

The reason for the high stability of one of the two isomers is still unknown. Examination of the literature dealing with the isomeric transformations of substituted benzoins established that in all instances the isomer containing, alongside the carbonyl, a group possessing a higher +M effect is more stable. For example:

$$n\text{-}(CH_3)_2NC_6H_4{-}CHOH{-}CO{-}C_6H_4Cl\text{-}n \longrightarrow n\text{-}(CH_3)_2NC_6H_4{-}CO{-}CHOH{-}C_6H_4Cl\text{-}n$$ [6]

$$n\text{-}CH_3O\text{-}C_6H_4\text{-}CHOH\text{-}CO\text{-}C_6H_5 \longrightarrow \longrightarrow n\text{-}CH_3OC_6H_4\text{-}CO\text{-}CHOH\text{-}C_6H_5.$$

This same cause is apparently responsible for the high stability of the isomer containing the group with the +M effect in the aliphatic-aromatic series as well: under the conditions in which methylbenzoylcarbinol is isomerized to phenylacetylcarbinol, p-methoxybenzoylcarbinol proves to be stable [7].

To get to the bottom of the influence of electronic effects of groups upon the quantitative proportions of the isomers of the alpha ketonic alcohols formed, it is worthwhile to get an idea of the mechanism of the isomerization reaction. We know that the isomerization of aliphatic-aromatic benzoins and alpha ketonic alcohols takes place readily in a weakly alkaline medium through an ene-diol as an intermediate product [8]. The sequence of transformations may be represented by the following diagram:

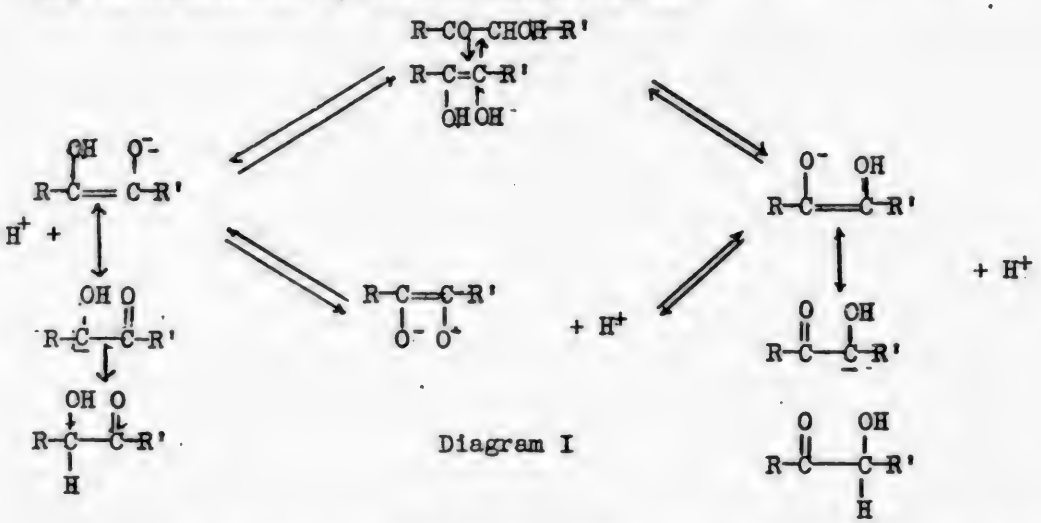
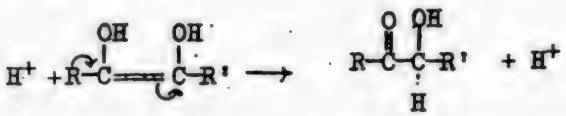


Diagram I

It is obvious from the above diagram that the greater the +M effect of the radical, the greater the electron density at the corresponding beta carbon atom in the ene-diol, which results in a lesser ionization of the hydrogen of the hydroxyl group attached to the same C atom, and in an easier coordination of the proton to the latter:



As a result, a ketonic alcohol is formed that contains the carbonyl group next to the radical that possesses a grouping with a greater +M effect.

It follows from investigation of the quantitative proportions of the isomers in an equilibrium mixture of the simplest aliphatic-aromatic alpha ketonic alcohols

$$C_6H_5CO\text{-}CHOH\text{-}CH_3 \rightleftharpoons C_6H_5CHOH\text{-}CO\text{-}CH_3$$
$$0\% \qquad\qquad 100\%$$

that in the ene-diol grouping the +M effect of CH_3 is higher than the +M effect of C_6H_5.

The smaller +M effect of the C_2H_5 group, due to the considerably lower degree of protonization of the hydrogen in the CH_2 group, results in a much lower

percentage of the ketonic alcohol containing a propionyl grouping in the equilibrium mixture.

Examination of the literature does not enable us to draw any conclusion whatsoever concerning the inductive effect of atoms and groups upon the mechanism of the isomeric transformations of alpha ketonic alcohols.

We set ourselves the problem of exploring the aliphatic-aromatic ketonic alcohols containing a halogen atom at the para position of the phenyl ring in order to develop the above-mentioned hypothesis still further and to ascertain the effect of substituents upon the isomeric transformations of alpha ketonic alcohols.

Of the halogen-substituted aliphatic-aromatic alpha ketonic alcohols, only n-Br—C_6H_4—CO—CHOH—CH_3, whose structure has been set down on the basis of its synthesis, has been described, while its chemical properties have not been studied [9].

The introduction of a chlorine or bromine atom at the para position ought to result in a lower electron density in the reaction zone, owing to the -J and +M effects of the latter (in our case, in the $-C(OH)=C(OH)-$ grouping, and in a certain relative increase of this density at the beta carbon atom with respect to the phenyl ring.

We resolved to investigate the effect of halogens upon para-chlorine-substituted phenyl methyl ketols.

In developing a method for synthesizing methyl-p-chloro-benzoylcarbinol, we came across an unusual course of the reaction, namely, the isomeric ketonic alcohol, which proved to be less stable and to be capable of turning into the ketonic alcohol that is the normal reaction product, if formed; the present paper is devoted to a description of this observation.

We proposed to synthesize the ketonic alcohol in the usual manner: by heating α-bromoethyl-p-chlorophenyl ketone with potassium formate in a methanol medium. We found, however, that the ketonic alcohol synthesized in this fashion was actually a mixture of two ketonic alcohols: methyl-p-chlorobenzoylcarbinol and p-chlorophenylacetylcarbinol. Formation of a mixture of ketols was proved in the usual manner: by converting them into the respective glycols and oxidizing the latter with lead tetraacetate.

The results of this experiment are shown in Diagram II.

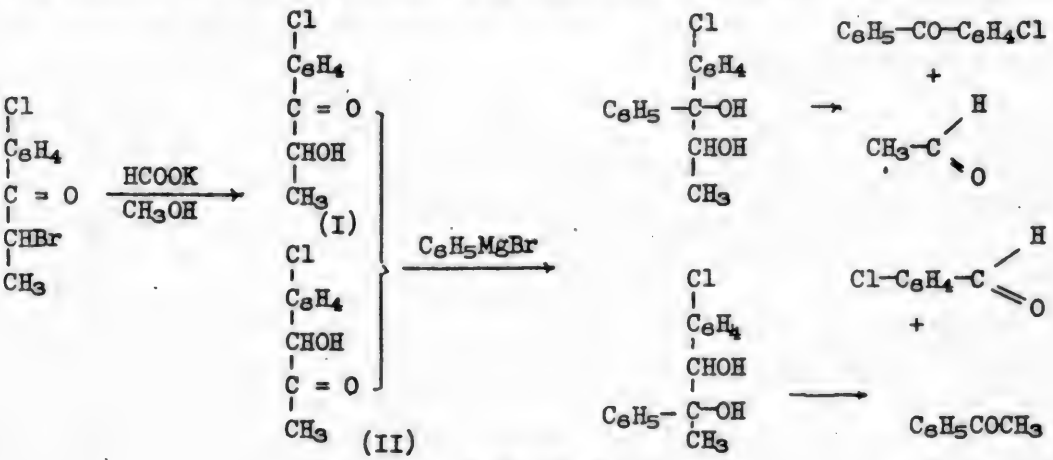
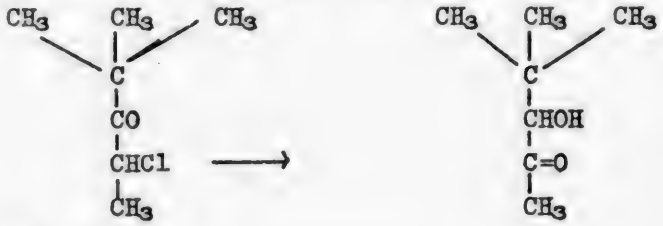


Diagram II

The two ketonic alcohols may be formed by the isomeric transformation of the normally formed ketol I.

Analogous processes involving the formation of isomeric ketonic alcohols when halogen ketones are heated with methanol and potassium formate have been observed by A. E. Favorsky, V. Vasilyev, and P. A. Ashmarin [10]:



and T. I. Temnikova [11]:

$$C_6H_5-CO-CHBr-CH_3 \longrightarrow C_6H_5-CHOH-CO-CH_3.$$

In both of these papers the isomeric ketonic alcohols were found to be more stable and could be produced by the isomeric transformation of the ketonic alcohols formed initially, which are the normal reaction products.

Investigation showed that in our instance the reverse phenomenon takes place: the normal reaction product—methyl-p-chlorobenzoylcarbinol—proves to be more stable, inasmuch as, under the conditions that facilitate the reciprocal transition of the isomeric ketonic alcohols (alcoholic alkali, heating to 100° with $BaCO_3$ and water), the mixture of ketonic alcohols yields pure methyl-p-chlorobenzoylcarbinol, as was likewise demonstrated by conversion of the latter into a glycol and oxidation of the glycol.

Thus, it follows from a comparison of the results of previous investigations with the present research that in nonnuclear-substituted ketonic alcohols the isomer containing an acetyl grouping is stable. When the chlorine atom is in the para position, the isomer containing a benzoyl grouping proves to be stable.

$$C_6H_5-CO-CHOH-CH_3 \longrightarrow C_6H_5-CHOH-CO-CH_3,$$

$$ClC_6H_4-CO-CHOH-CH_3 \longleftarrow ClC_6H_4-CHOH-CO-CH_3.$$

It follows, therefore, that introducing chlorine at the para position of the phenyl ring is enough for the ratio of the +M effects in the ene-diol to be reversed:

$$Cl-C_6H_4 > CH_3$$

$$C_6H_5 < CH_3$$

The inductive effect of the chlorine ought to affect the velocity of reciprocal conversion of both ketonic alcohols, as tautomeric transformations involving a shift of a hydrogen atom during alkaline catalysis take place the more readily, the higher the protonization of the latter.

What is particularly noteworthy is that in the bromoketone synthesis, the isomeric ketonic alcohol (II), which is an anomalous reaction product and readily converts into the expected ketol, is formed alongside the normal product (I)

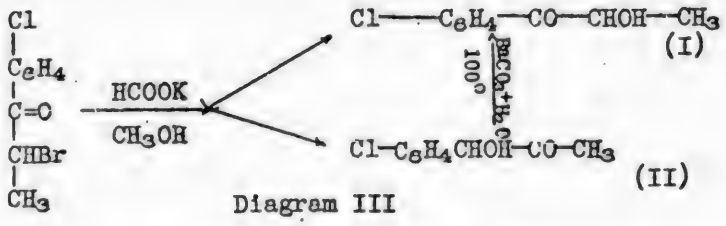


Diagram III

In this instance, as in several others [12], the reaction is anomalous, resulting in the formation of a product that is less stable energetically. The reasons for the formation of an isomeric ketonic alcohol must evidently be sought in the mechanism of the transition from the bromoketone to the ketonic alcohol.

The process of formation of the ketonic alcohol from the bromoketone when the latter is reacted with potassium formate in methanol consists of several stages:

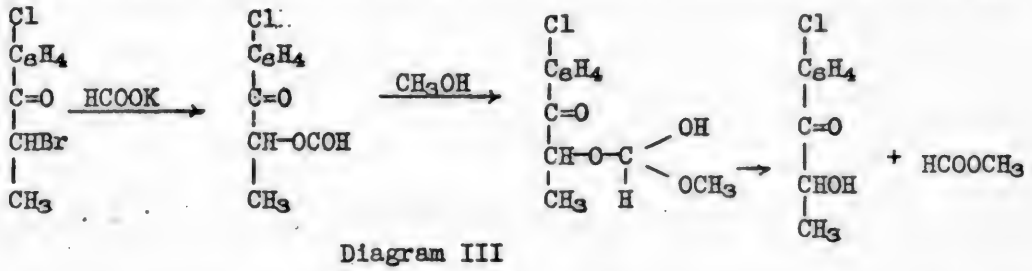
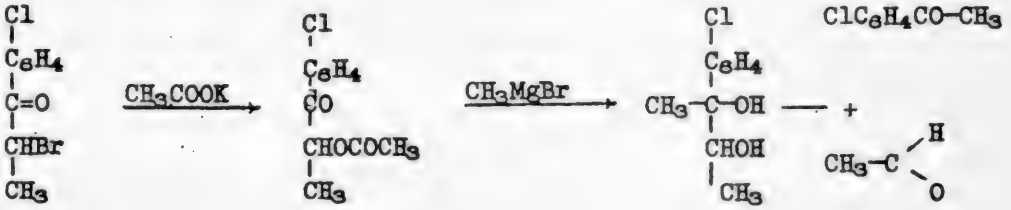


Diagram III

We were interested in learning in exactly which of these stages the isomeric conversion takes place, with the formation of the isomeric ketonic alcohol (II) as the end result.

To explore this problem, we studied the initial stage—the stage in which an ester is formed—using as our example the reaction of α-bromoethyl-p-chlorophenyl ketone with potassium acetate. When α-bromoketones are reacted with salts of organic acids, it is often found that, besides the normal trend of the reaction, anomalous products are formed: esters corresponding to the isomeric ketonic alcohols [13]. Here, too, it was found that the reaction can go in two directions.

The acetic ester was prepared by heating the bromoketone with potassium acetate in an alcoholic solution. The structure of the ester synthesized was determined by converting it into a glycol by reacting it with CH_3MgBr and then oxidizing the glycol. This resulted in synthesis of p-chloroacetophenone and acetic anhydride. Careful analysis of the oxidation products indicated that no acetone was present.



It has thus been established that the reaction of α-bromoethyl-p-chlorophenyl ketone with potassium acetate yields only the normal reaction product – the acetate of methyl-p-chlorobenzoylcarbinol. It must be supposed that, similarly, when the same bromoketone is reacted with potassium formate, the formic ester formed in accordance with Diagram III corresponds to methyl-p-chlorobenzoylcarbinol. Evidently, the isomeric conversion takes place during the re-esterification state.

In the literature we find no references to observations of molecular rearrangements during re-esterification processes. On the contrary, this reaction is one of the mildest methods of rupturing the ester bond and is often employed to indicate the structure of a substance.

Our research is continuing in order to elucidate the mechanism of the re-esterification reaction and the factors that result in molecular rearrangement.

When α-bromoethyl-p-chlorophenyl ketone is reacted with potassium benzoate, the sole reaction product is a beautifully crystalline ester, with a m.p. of 92-93°. The benzoic ester proved to be extremely resistant to alkaline saponification. The ester was recovered unchanged after 30 hours of heating to 100-110° with freshly precipitated $BaCO_3$ and water.

It is worthy of note that introducing a chlorine atom at the para position of the benzene ring resulted in a higher reactivity of the carbonyl group. Methyl-p-chlorobenzoylcarbinol differs from methylbenzoylcarbinol, which does not form characteristic carbonyl group derivatives, in that it readily forms a semicarbazone.

EXPERIMENTAL

I. Synthesis of Ethyl-p-chlorophenyl Ketone

The initial ethyl-p-chlorophenyl ketone was synthesized by a somewhat modified Collet method [14].

A solution of 50 g of chlorobenzene and 50 g of propionyl chloride was slowly added to 116 g of freshly sublimed $AlCl_3$ in 100 ml of CS_2, with constant stirring. The reaction mixture was set aside for two days and then heated for 3 hours over a water bath, after which the coordination compound was decomposed by pouring it over ice. The ketone was purified by steam distillation, subsequently partially hardening into a waxy mass. The yield was 68 g or 91% of the theoretical. The m.p. was 34-36°; according to Collet, ethyl-p-chlorophenyl ketone has a m.p. of 35-36°.

II. Synthesis of α-Bromoethyl-p-chlorophenyl Ketone

58 g of bromine was added drop by drop to 61.2 g of the ketone in 180 ml of CH_3COOH. The decolorizing of the bromine was observed a few minutes after the first few drops of bromine were added. After all the bromine had been added and no more HBr was evolved, the dark-brown solution was poured into water, the bromoketone separating out in crystalline form. In some cases the bromoketone was observed to crystallize in the reaction vessel. In all instances, however, the substance was dissolved in ether, dried with $MgSO_4$, and recrystallized from ligroin after the ether had been driven off. M.p. 77-79°. The yield was 80-90% of the theoretical. The bromoketone is a finely crystalline substance, with a lustrous gray sheen; it severely irritates the mucous membrane and the skin.

Collet gives the m.p. of α-bromoethyl phenyl ketone synthesized from α-bromopropionyl and chlorobenzene by a Friedel Crafts reaction as 77.5° [13].

III. Synthesis of Methyl-p-chlorobenzoylcarbinol

1. Reaction of α-Bromoethyl-p-chlorophenylKetone with Potassium Formate in a Methanol Medium

13 g of the bromoketone was heated with 10 g of potassium formate and 35 ml of methanol in sealed tubes to 128-130° for 8 hours. After the tubes were opened, the reaction product was treated in the usual manner. After the ether had been driven off (the ether solution having been desiccated with $MgSO_4$), the product was recovered by fractionation as a transparent, very slightly greenish oil with a b.p. of 138-139° at 9.5 mm. The yield was 4.3 g.

$d_4^{19.5}$ 1.235; n_α^{18} 1.5497; n_β^{18} 1.5683; n_α^{19} 1.5472, MR_α 47.36.

$C_9H_9O_2ClF_3$. Calculated: MR_α 46.25.

0.1000 g substance: 0.0780 g AgCl.
0.1436 g substance: 0.1132 g AgCl.
0.1009 g substance: 0.2160 g CO_2; 0.0443 g H_2O.
0.1836 g substance: 0.3945 g CO_2; 0.0895 g H_2O.
Found %: C 58.39, 58.59; H 4.91, 5.45; Cl 19.3, 19.5.
$C_9H_9O_2Cl$. Calculated %: C 58.54; H 4.88 Cl 19.24

When this substance was mixed with a semicarbazide solution, the semicarbazone soon began to settle out; it fused at 183-184° in a sealed capillary after recrystallization from absolute alcohol.

0.1030 g substance: 15.2 ml N_2 (16.5°, 755 mm).
0.1013 g substance; 15.2 ml N_2 (16.5°, 755 mm).
Found %: N 17.47, 17.38.
$C_{10}H_{12}N_2O_2Cl$. Calculated %: N 17.4.

Action of phenylmagnesium bromide upon the reaction product. A solution of 4 g of the substance in 25 ml of ether was added to a CH_3MgBr solution, prepared with 1.6 g of Mg. The mixture was allowed to stand overnight, and then it was heated for 3 hours over a water bath; after decomposition with water, the ethereal solution was mixed with basic magnesium salts, and the residue after the ether had been driven off was treated with steam to eliminate impurities. The oily product obtained was extracted with ether. The ethereal solution was desiccated with $MgSO_4$. The oil recovered after the ether was driven off was dissolved in an equal quantity of ligroin, causing the substance to precipitate in crystalline form. After the ligroin had been driven off, the residue was converted into the crystalline state by precipitating the tar from an alcoholic solution with water, followed by the usual crystallization of the residue from ligroin. A total of 2 g of a substance with a m.p. of 74-81° was recovered as spherical white crystals.

The substance turns concentrated H_2SO_4 violet.

The crystals of both batches were subjected to analysis.

0.1240 g substance: 0.3096 g CO_2; 0.0670 g H_2O.
0.1093 g substance: 0.2737 g CO_2; 0.0588 g H_2O.
0.1061 g substance: 0.0587 g AgCl.
0.1062 g substance: 0.0580 g AgCl.
Found %: C 68.1, 68.31; H 6.05, 6.02; Cl 13.74, 1352
$C_{15}H_{15}O_2Cl$. Calculated %: C 68.57; H 5.72. Cl 13.52.

0.1079 g substance: 21.5 g benzene: Δt 0.094.
Found: M 274.
$C_{15}H_{15}O_2Cl$. Calculated: M 262.5.

Oxidation of the glycol was effected with lead tetraacetate by the method described in detail in the paper by T.I.Temnikova and B.F.Martynov [15]. We took 1 g of the substance, 5 g of $(CH_3COO)_4Pb$, and 15 ml of glacial acetic acid, carefully purified and distilled with $KMnO_4$. No light volatile oxidation products were found. The neutral products were driven off with steam, the first substance passing

over being an oil, followed by crystals that proved to be p-chlorobenzophenone. For the sake of comparison, p-chlorobenzophenone was prepared from benzoyl chloride, chlorobenzene, and $AlCl_3$; both the known ketone and that produced by oxidation fused at 72-73° and exhibited no depression of the melting point when mixed into a test sample. Wegerhoff gives 77-79° as the melting point of p-chlorobenzophenone [18].

The emulsion from which the p-chlorobenzophenone was isolated exhibited a positive reaction for aldehydes; it was oxidized in the cold with ammoniacal silver nitrate for 40 hours. After the whole had been acidulated with H_2SO_4, it was steam distilled again, yielding some more solid chlorobenzophenone and acetophenone; the latter was identified as its semicarbazone with a m.p. of 198-200°. A mixed test sample exhibited no depression of the melting point. Oxidation resulted in approximately equal amounts of acetophenone and the chlorobenzophenone. Moreover, p-chlorobenzoic acid, with a m.p. of 233-235°, was isolated from the residue left behind when the ketones were distilled off, as well as from the lead salts; the acid was purified by recrystallization from a mixture of absolute ether and absolute alcohol with ensuing distillation. The result of oxidation indicates that a mixture of isomeric ketonic alcohols was synthesized.]

2. Synthesis of Methyl-p-chlorobenzoylcarbinol by Isomerizing a Mixture of Ketonic Alcohols

a) Isomerization by $BaCO_3$ and Water

The oil recovered after the reaction with HCOOK was performed and the ether driven off was heated over a boiling water bath without further purification for 30 hours with water and freshly precipitated $BaCO_3$. The reaction product was extracted with ether, and the ether extract desiccated with $MgSO_4$. After the ether had been driven off the residue was distilled in vacuum. The major fraction distilled over at 150-152° at 15 mm. The yield of the fraction was 46% of the theoretical based on the initial bromoketone.

$d_4^{21.5}$ 1.2365; $n_\alpha^{21.5}$ 1.54738; MR_α 47.35.

$C_9H_9O_2ClF_3$. Calculated MR_α 46.25.

Mixture with a semicarbazide solution precipitated the semicarbazone, with a m.p. of 186-188° (in a sealed capillary).

0.0972 g substance: 14.1 ml N_2 (20°, 774.5 mm).
0.1078 g substance: 15.7 ml N_2 (18°, 771.1 mm).
Found %: N 17.05, 17.20.
$C_{10}H_{12}O_2N_2Cl$. Calculated %: N 17.4.

When the substance was reacted with phenylmagnesium bromide, we got a glycol with a m.p. of 88.5-89.5°.

0.1054 g substance: 0.0574 g AgCl.
Found %: Cl 13.48.
$C_{15}H_{15}O_2Cl$. Calculated %: Cl 13.52.

The glycol was oxidized with lead tetraacetate. Oxidation yielded the p-nitro phenylhydrazone of acetic anhydride, with a m.p. of 117-119° and p-chlorobenzophenone; no other oxidation products were found.

b. Isomerization by an Alcoholic Alkali

The oil synthesized by reacting 40 g of α-bromo-p-chlorophenyl ketone and 25 g of HCOOK was isomerized with an alcoholic alkali. The oil was dissolved in a 1.7% solution of KOH in alcohol. The color turned cherry-red immediately, but it grew lighter after two days had passed. Three days later, the solution was saturated

with CO_2 and the K_2CO_3 was separated out. After the alcohol had been driven off the residue was poured into water, the oil extracted with ether, the extract desiccated with $MgSO_4$, the ether driven off, and the remaining residue distilled. This yielded 4.7 g of a substance with a b.p. of 134-134.5° at 7.5 mm. The residue contained a large amount of tar. When the oil was left to stand, a small quantity of white acicular crystals with a m.p. of 225-231° separated out; apparently this was p-chlorobenzoic acid.

The substance was identical with that obtained in the preceding experiment, treated with phenylmagnesium bromide. It yielded a glycol with a m.p. of 84-86°.

0.1007 g substance: 0.0552 g AgCl.
Found %: Cl 13.57.
$C_{15}H_{15}O_2Cl$. Calculated %: Cl 13.52.

The glycol was oxidized with lead tetraacetate. Oxidation yielded p-chlorobenzophenone and traces of acetophenone.

IV. Synthesis of the Acetate of Methyl-p-chlorobenzoylcarbinol

25 g of α-bromoethyl-p-chlorophenylketone, 12 g of CH_3COOK, and 50 ml of ethyl alcohol were heated for 5 hours over a water bath to the alcohol's boiling point. The reaction was complete after 5 hours. The substance synthesized was distilled in vacuum after the usual preliminary treatment. This yielded 10 g of a substance with a b.p. of 123-125° at 1 mm. The yield was 43.5% of theory.

d_4^{20} 1.216; n_α^{20} 1.5236; MR_α 56.94.

$C_{11}H_{11}O_3ClF_3$. Calculated MR_α 55.57.

0.1265 g substance: 0.0790 g AgCl.
0.1658 g substance: 0.1090 g AgCl.
Found %: Cl 15.46, 15.38.
$C_{11}H_{11}O_3Cl$. Calculated %: Cl 15.66.

Proof of the Structure of the Synthesized Substance

Reaction with CH_3MgBr. Synthesis of 1-methyl-1-p-chlorophenylpropanediol-1,2. 7.5 g of the acetate was added drop by drop to a Grignard reagent, prepared with 7.7 g of Mg and CH_3Br. After standing for 12 hours and boiling for 6 hours, the organomagensium coordination compound was decomposed by ice water. The ethereal solution was mixed with basic magnesium salts, desiccated with $MgSO_4$, and distilled. This yielded 3.5 g of a substance that boiled at 125° at 1 mm.

0.1593 g substance: 0.1130 g AgCl.
0.1286 g substance: 0.0924 g AgCl.
Found %: Cl 17.56, 17.80.
$C_{10}H_{13}O_2Cl$. Calculated %: Cl 17.70.

The glycol was oxidized with lead tetraacetate, using 2.5 g of the glycol. Oxidation was effected in apparatus with ground-glass seals. The light volatile products were poured into ice water; they were expected to include acetaldehyde and acetone. The former was readily distinguishable by its odor. As it was extremely important to ascertain whether acetone had been produced by this oxidation, the acetaldehyde was not identified as such, but the aqueous solution was oxidized with ammoniacal silver nitrate. No neutral products – ketones – were found after the aldehydes had been oxidized.

The less volatile neutral products were driven from the reaction flask with

steam. The distillate exhibited a negative reaction for aldehydes. The emulsion was treated with semicarbazide solution, yielding 1.2 g of the pure semicarbazone, with a m.p. of 191-192°, which is the melting point of the semicarbazone of p-chloroacetophenone. A test sample mixed with specially prepared semicarbazone of p-chloroacetophenone fused at 191-193°. Nor was p-chlorobenzoic acid found among the oxidation products.

The semicarbazone of p-chloroacetophenone has not been described in the literature. We prepared it from p-chloroacetophenone, produced by the standard method [17] but using twice the amount of $AlCl_3$. The b.p. of the ketone was 115-117° at 18 mm; the yield was 73% of the theoretical.

The semicarbazone consists of small, transparent, barely greenish crystals; m.p. 192-194°.

0.1070 g substance: 18.9 ml N_2 (20°, 764.3 mm).
0.1300 g substance: 22.5 ml N_2 (17°, 753.5 mm).
Found %: N 20.20, 20.07.
$C_9H_{10}ON_3Cl$. Calculated %: N 19.85.

V. Synthesis of the Benzoate of Methyl-p-chlorobenzoylcarbinol.

5 g of α-bromoethyl-p-chlorophenyl ketone was heated for 10 hours with 10 g of potassium benzoate dissolved in ethyl alcohol. The benzoic ester consists of colorless, large, prismatic crystals, which settle out as the ether solution is evaporated. This yielded 4 g of the substance, with a m.p. of 92-93.5° after recrystallization from petroleum ether.

0.1779 g substance: 0.0888 g AgCl.
0.1376 g substance: 0.0686 g AgCl.
Found %: Cl 12.39, 12.34.
$C_{18}H_{13}O_3Cl$. Calculated %: Cl 12.30.

The benzoic ester is unaffected by a boiling aqueous solution of $BaCO_3$; it underwent no change during 30 hours of this treatment.

SUMMARY

1. It has been demonstrated that a mixture of ketonic alcohols: methyl-p-chlorobenzoylcarbinol and p-chlorophenylacetylcarbinol, results from the reaction of α-bromoethyl-p-chlorophenyl ketone and potassium formate.

2. Heating the above mixture of ketonic alcohols to 100° with $BaCO_3$ and water isomerizes the p-chlorophenylacetylcarbinol, yielding pure methyl-p-chlorobenzoylcarbinol.

3. Thus, it has been shown that the anomalous reaction product, p-chlorophenyl acetylcarbinol, formed during the synthesis of the α-ketonic alcohol is an unstable substance and is isomerized to the normal reaction product, methyl-p-chlorobenzoylcarbinol, under conditions that facilitate the reciprocal conversion of the ketonic alcohols. The isomeric conversion occurs, apparently, during the re-esterification stage.

4. The reaction of α-bromoethyl-p-chlorophenylcarbinol with potassium acetate results in the formation of only one ester, the structure of which corresponds to the initial ketone.

5. The diagram of the mechanism of the isomeric transformation of alpha ketonic alcohols in aqueous solution is given. It follows from the research data that the +M effect of the p-chlorophenyl is higher than that of the methyl group in the intermediate product formed during the rearrangement, the corresponding ene-diol.

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THE PROBLEM OF THE STRUCTURE AND TRANSFORMATIONS OF DIAZO COMPOUNDS

IX. DIRECTION AND RATE OF TAUTOMERIC CHANGES IN THE GROUP OF DIAZO COMPOUNDS *

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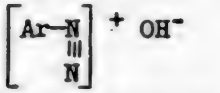
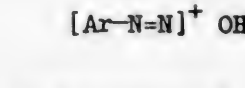
It seems quite obvious, from Le Chatelier's law, that as the external conditions (pH of the medium, temperature, etc.) change, the tautomeric equilibrium in any system ought to shift toward the formation of compounds that are favored energetically under the given conditions. That is why the tautomeric equilibrium of two acids shifts toward the formation of the weak acid, if they are present in the free state, and toward the formation of the strong acid if they are present as salts. The same may be said of the equilibrium in a system consisting of two tautomeric bases or their salts. If they are present in the free state, the equilibrium is shifted toward the formation of the weak base, whereas if they are present as salts, it is shifted toward the formation of the strong base.

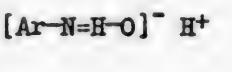
The changes observed by us [1] may be easily explained from this point of view. At bottom, we have established [2], in many diazo compounds investigated by means of a glass electrode, that all salts of diazo compounds are formed from two bases and two acids:



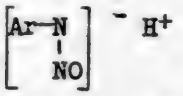
Diazonium hydroxide



Diazohydroxide



Diazotic acid



Nitrosamino acid

The numerical values of the dissociation constants, determined for diazo compounds whose properties differ, were found to lie within the following range:

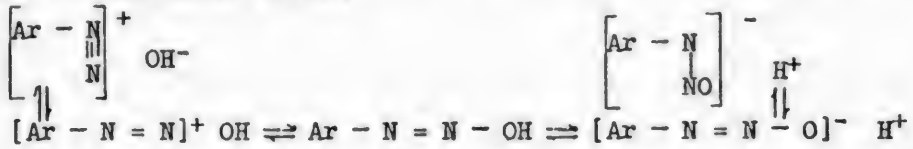
Diazonium hydroxide.....	K_b'	from 10^{-6} to $10^{-2.5}$
Diazohydroxide.....	K_b''	from $10^{-6.5}$ to $10^{-4.5}$
Diazotic acid.....	K_a''	from $10^{-8.5}$ to 10^{-12}
Nitrosamino acid.....	K_a'	from 10^{-6} to $10^{-7.5}$

That is, it has been found that diazonium hydroxide, as a base, is several times as strong as diazohydroxide, and that nitrosamino cid is stronger than diazotic acid by an even greater factor.

Hence, bearing in mind the strength of the bases and acids as well as the

* Cf. Report VIII [2]. Z. N. Slavnaya took part in the experimental work involved.

simple rules for the course of tautomeric changes cited above, we may expect a system containing two tautomeric bases in equilibrium to contain an amphoteric diazohydrate and two tautomeric acids:



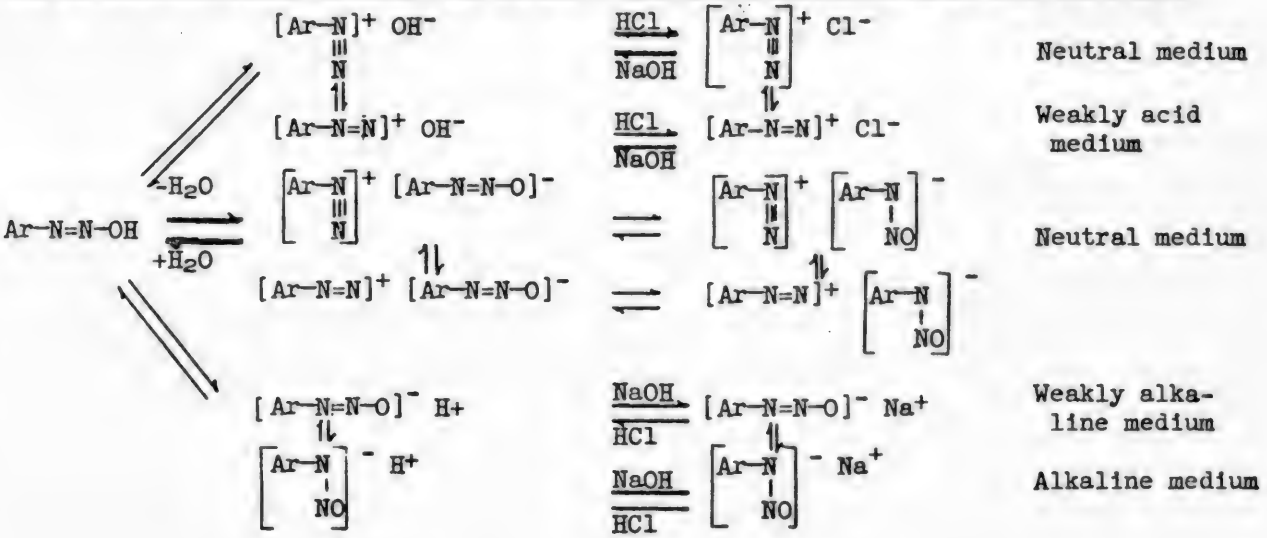
with the equilibrium shifted to the right in an alkaline medium (toward the formation of sodium nitrosaminate), and to the left in an acid medium (toward the formation of diazonium chloride). Or, putting it more simply, of the three possible structures of diazo compounds: diazonium, diazo, and nitroamine, the first will predominate in an acid medium, the second in a neutral medium, and the third in an alkaline medium [3].

In fact, when p-nitrobenzenediazonium chloride, for example, is gradually alkalized, more and more of a compound is formed containing a cation of diazo structure and an anion of nitrosamine structure. The diazonium chloride gives rise to a diazo chloride, and the diazonium hydroxide to the less ionized diazo hydroxide. The latter compound gives rise to the diazo diazoate, via the amphoteric diazohydrate, further alkalization producing sodium diazoate. But since the nitrosamino acid is a stronger acid than the diazotic acid, the diazodiazoate or sodium diazoate will turn into the diazo nitrosaminate or the sodium nitrosaminate, respectively.

The converse is true when "nitrosamine red" is gradually acidulated. Compounds with a nitrosamine structure vanish, and compounds with diazo, and then with diazonium, structure begin to make their appearance. The nitrosamino acid formed during acidulation is converted into a weaker diazotic acid, and then, via the diazohydrate, into a diazonitrosaminate, and finally into a diazonium chloride upon further acidulation.

A diagram of the tautomeric changes of diazo compounds as a function of the pH of the medium is given below. The predominant directions of the changes are shown by heavy arrows in the diagram.

Diagram of the Tautomeric Changes of Diazo Compounds With the pH of the Medium



The constants of tautomeric equilibrium of free bases and acids of diazo compounds may be computed from their dissociation constants in the same way as is done, for instance, for the nitroparaffins [4]. The following method seems to us to be no less simple and correct.

Let H denote the hydrogen-ion concentration in an equilibrium mixture of the sodium salts of any two tautomeric acids; then from the well-known equations:

$$H = \sqrt{\frac{K_w K_a'}{C_1}}, \qquad H = \sqrt{\frac{K_w K_a''}{C_2}},$$

where K_a' and K_a'' are the dissociation constants of the acids and C_1 and C_2 are the salt concentrations in the equilibrium mixture, it follows that:

$$\frac{K_a'}{K_a''} = \frac{C_1}{C_2}. \tag{1}$$

Hence, the concentration of the sodium salt of each of the tautomeric acids in the equilibrium mixture is a linear function of the magnitude of the acid dissociation constant. This is not surprising, since we know, for example, that when an alkali is added to a mixture of two acids, the alkali is distributed between them in proportion to their strength, [5].

In the tautomeric equilibrium of the hydrochlorides of two bases, we may similarly prove that:

$$\frac{K_b'}{K_b''} = \frac{C_1}{C_2} \tag{2}$$

where K_b' and K_b'' are the dissociation constants of the bases and C_1 and C_2 are the salt concentrations in the equilibrium mixtures.

When two free acids are in tautomeric equilibrium, it follows from the equations

$$H = \sqrt{K_a' C_1} = \sqrt{K_a'' C_2}$$

that

$$\frac{K_a'}{K_a''} = \frac{C_2}{C_1}. \tag{3}$$

Similarly, for two free bases:

$$\frac{K_b'}{K_b''} = \frac{C_2}{C_1} \tag{4}$$

Equations (1), (2), (3), and (4) make it possible to gain a quite exact notion of the composition of equilibrium mixtures of tautomeric acids, bases, or salts.

For example, it follows from (1) that in an equilibrium mixture of the sodium salts of nitrosamino and diazotic acids, the salt of the former acid will predominate, since it is the stronger acid. This predominance is reinforced in the presence of excess alkali and, vice versa, it is diminished as a mineral acid is added or as the sodium cation is replaced by another cation belonging to a base that is weaker than sodium hydroxide. According to (3), the diazotic acid will predominate in an equilibrium mixture of free acids.

It follows from (2) that in an equilibrium mixture of hydrochlorides of diazo compounds, the diazonium chloride will predominate. The proportion of the diazonium structure will increase as the excess hydrochloric acid in the solution rises, and it will decrease as alkali is added or the anion of hydrochloric acid is

replaced by the anion of a weak acid. In the case of free bases, according to (4), the diazo structure of the cation of diazo compounds will predominate.

An increase in the acidity or a decrease in the alkalinity of diazo compounds depends on the nature of the substituent attached to the diazo compound's aromatic ring, in the following sequence:

$$OCH_3,\ CH_3,\ H,\ Cl,\ SO_3Na,\ NO_2.$$

According to (1), (2), (3), and (4), the ratio of diazoate to the nitrosaminate in an equilibrium mixture of salts of the two acids, or the ratio of the diazo salt to the diazonium salt in an equilibrium mixture of salts of diazo compounds with the acid, increases in the same sequence, namely, from p-diazoanisole to p-nitrodiazobenzene.

All this agrees well with the known facts. In particular, it fully explains the pattern of the influence of the nature of the substituent in the diazo compound's aromatic ring observed by Hantzsch [8] and M.I.Rozova [7], and the influence of the nature of the ion linked to the ion of the diazo compound, upon the shift of the tautomeric equilibrium of salts of diazo compound salts to one side or the other.

In the present report we shall describe experiments on the tautomeric changes of 2-nitro, 4-nitro, 2-methyl-4-nitro, 2-methoxy-4-nitro, and 4-sulfodiazobenzenes.

In these experiments, the same changes and reactions of the same sort have been observed as in those described earlier [8]. Thus, spontaneous changes of the sodium diazoate into the sodium nitrosaminate, of the diazodiazoate into the diazonitrosaminate, and of a nitrosamino acid into the same diazonitrosaminate are reversible reactions of the first order.

The conversion of a diazonitroaminate or of a nitrosamino acid into a diazonium chloride is a pseudomonomolecular reaction, the rate of which grows with an increase in the hydrogen-ion concentration.

The relationship between the velocity constant, the activation energy, and the temperature in conversions of p-nitrodiazobenzene is expressed by the following equations, based on refined data:

Diazonium chloride from the nitrosamine in the presence of excess HCl (pH = 5.6)..... $K = 51.6 - 30900/RT$

Diazonium chloride from the nitrosamine in the presence of excess HCl (pH = 1.9)..... $K = 38.7 - 23200/RT$

Sodium nitrosaminate from the sodium diazoate..... $K = 53.3 - 30700/RT$

Diazonitrosaminate from the diazodiazoate..... $K = 53.8 - 30900/RT$

Our data, especially the equality of the activation energies, are beautifully explained by a shift to one side or the other, under the influence of an alkali or an acid, of the same equilibrium system of free diazo compounds cited above. In the case of nitrodiazobenzenes, all changes in such a system occur practically instantaneously and, hence, with a low value of the activation energy. Only the tautomeric change of a diazotic acid into a nitrosamino acid in an alkaline medium, or the converse change in an acid medium, takes place at a reduced rate and, hence, with a high value of activation energy (this is 30,900 cal per degree for p-nitrodiazobenzene).

According to Hantzch and Gerilowski [9], the conversion of p-sulfodiazobenzene exhibits its "singularities," which bear out the correctness of the stereoisomeric hypothesis re the structure of diazo compounds. According to them, when an equivalent quantity of an alkali is added to an inner salt of p-sulfobenzenediazonium, the diazonium hydroxide is formed, exhibiting an alkaline reaction, which gradually

regroups into a neutral syndiazohydrate.

If this were correct, the addition of alkali in a slightly more than equivalent amount should result in the presence of excess alkali, since the diazonium hydroxide does not react with the alkali. But our very first experiments showed that no excess alkali is found at all under these conditions, excess alkali appearing only when twice as much alkali is added as is required to isolate the diazonium hydroxide.

Further researches [2] on conversions of p-sulfodiazobenzene indicate that they do not differ in principle in any way from the changes of p-nitrodiazobenzene or of other diazo compounds. The titration curves of p-sulfodiazobenzene are quite like the titration curves of other diazo compounds, differing regularly only in the pH values at corresponding points.

We reproduce below data for p-sulfodiazobenzene on measurements of the rate of spontaneous change of a weakly alkaline diazodiazoate (pH = 10) into the diazonitrosaminate (pH = 8) at 5° and the rate of the spontaneous change of the nitrosamino acid into the diazonitrosaminate at the same temperature.

EXPERIMENTAL

Spontaneous Change of a Sodium Diazoate into a Sodium Nitrosaminate

10 ml of a solution of o-nitrobenzenediazonium chloride, and 90 ml of water were titrated at 10° with 0.1 N NaOH. The consumption of 0.1 N NaOH in titration was 8.6 ml up to the equivalence point at a pH of 5.3 (neutralization of the excess hydrochloric acid) and 27.8 ml up to the equivalence point at a pH of 10.4 (neutralization of the diazo compound).

62 ml of water was added to 10 ml of the same solution of the diazonium chloride, and 27.8 ml of 0.1 N NaOH was then added all in one batch. The resulting solution of the sodium diazoate was stirred at 10°, with atmospheric carbon dioxide excluded, for 1, 5, 10, 15, and 20 minutes, and then rapidly titrated with 0.1 N HCl. The logarithmic concentration of the sodium diazoate as a function of the duration of the reaction is shown in Fig. 1 for ortho and para nitrodiazobenzenes and for 2-methyl-4-nitrodiazobenzene.

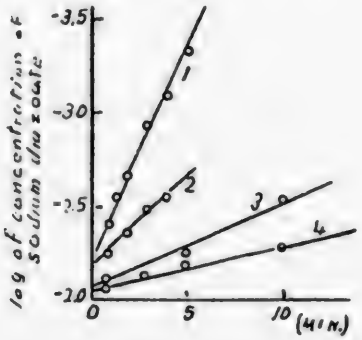


Fig. 1. Rate of conversion of the sodium diazoate into the sodium nitrosaminate at 10°.

1 - 4-Nitrodiazobenzene at 13°;
2 - 4-nitrodiazobenzene at 10°;
3 - 2-methyl-4-nitrodiazobenzene at 10°;
4 - 2-nitrodiazobenzene at 10°.

Spontaneous Change of the Diazodiazoate Into the Diazonitrosaminate

10 ml of a solution of o-nitrobenzenediazonium and 90 ml of water were titrated with 0.1 N NaOH at 10°. The consumption of alkali was 9.0 ml up to the first equivalence point, and 28.6 ml up to the second point.

71 ml of water was added to the same solution of the diazonium chloride, and 18.8 ml of 0.1 N NaOH was then added at once. The resulting solution of the diazodiazoate, which was weakly alkaline at first, was stirred at 10°, gradually becoming neutral.

The concentration of the diazodiazoate was determined at 1, 5, 10, 15, and 20 minutes by titration with 0.1 N HCl. The relationship between the logarithm of the diazodiazoate concentration and the duration of the reaction is shown in Fig. 2.

The data for p-nitrodiazobenzene and for 2-methyl- and 2-methoxy-4-nitrodiazobenzene obtained in the same way are reproduced there as well.

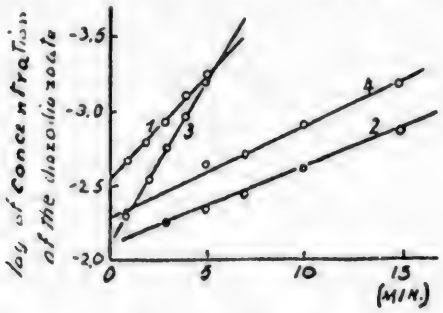


Fig. 2. Rate of change of the diazodiazoate into the diazonitrosaminate at 10°.

1 -4-Nitrodiazobenzene; 2 - 2-methyl-4-nitrodiazobenzene; 3 - 2-methoxy-4-nitrodiazobenzene; 4 - 2-nitrodiazobenzene.

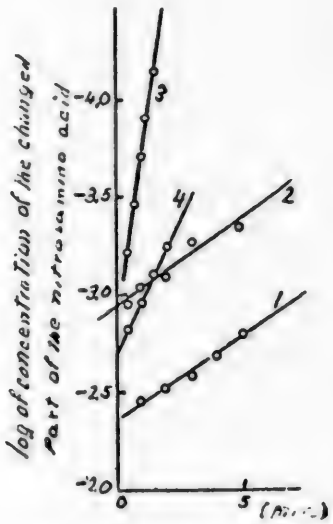


Fig. 3. Rate of change of the nitrosamino acid into the diazonitrosaminate.

1 - 4-nitrodiazobenzene at 13°;
2 - 2-methyl-4-nitrodiazobenzene at 15°;
3 - 2-methoxy-4-nitrodiazobenzene at 15°;
4 - 2-nitrodiazobenzene at 10°.

Spontaneous Change of the Nitrosamino Acid into the Diazonitrosaminate

240 ml of water and an equimolecular quantity of 0.1 N HCl were added to 10 ml of 0.1 N 2-methoxy-4-nitrodiazobenzene. The resulting solution of the nitrosamino acid, containing no free hydrochloric acid, was acid at first (pH = 4), but it turned weakly alkaline within 5 minutes (the pH value rose spontaneously to 8.05, after which it remained constant.

The concentration of the nitrosamino acid was determined at 1, 2, 3, 4, and 5 minutes by titration with 0.1 N HCl.

As the duration of the reaction is increased, the consumption of hydrochloric acid from one equivalence point (pH of 7.8) to another (pH of 4.3) increases from zero to half the equivalence for each equivalent of the diazo compound.

Similar experiments were made with other nitrodiazobenzenes. The relationship between the concentration logarithm of the changing portion of the nitrosamino acid and the length of the reaction is shown in Fig. 3.

Change of the Nitrosamino Acid into the Diazonium Chloride When Acted Upon by Hydrochloric Acid

The concentration of the sodium nitrosaminate solution and its percentage of excess alkali were determined by preliminary acidimetric titration.

Enough 0.1 N HCl was added at one time to 25 ml of the sodium nitrosaminate solution and 80 ml of water to make the pH 5.6. This pH value was then kept constant at 15° by adding 0.5 ml of 0.1 N HCl from time to time.

After the lapse of an accurately measured interval of time, the solution was rapidly titrated with 0.1 N HCl.

As the length of the reaction of hydrochloric acid with the nitrosamino acid

is increased (pH = 5.6), the consumption of hydrochloric acid gradually rises to the equivalent value.

The relationship between the logarithm of the concentration of the nitrosamino acid and the length of the reaction at 15° and a pH of 5.6 is shown in Fig. 4.

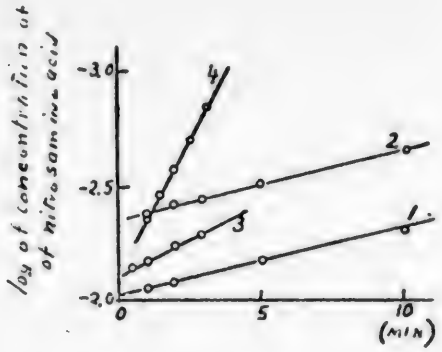


Fig. 4. Rate of change of the nitrosamino acid into the diazonium chloride at 15° and a pH of 5.6.

1 - 4-nitrodiazobenzene;
2 - 2-methyl-4-nitrodiazobenzene;
3 - 2-methoxy-4-nitrodiazobenzene;
4 - 2-nitrodiazobenzene

Spontaneous Change of p-Sulfodiazobenzene

100 ml of an acid solution of p-sulfobenzene was titrated at 5° with 0.1 N NaOH. The consumption of alkali in titration to the equivalence points was 5.0 and 22.5 ml.

13.7 ml of 0.1 N NaOH was added to 100 ml of the same solution. The resulting weakly alkaline solution of the diazodiazoate was stirred at 5°, and after some time titrated with 0.1 N HCl and NaOH.

0.25 g of pure sodium p-sulfobenzenenitrosaminate was dissolved in 100 ml of water. 10 ml of 0.1 N HCl was added, and the solution was titrated with 0.1 N HCl at 5° at 10, 20, and 30 minutes of stirring.

Fig. 5 shows the results of measurement of the kinetics of both conversions.

Velocity Constants of Changes of Nitro- and Sulfodiazobenzenes

Kind of change	Name of diazo compound	Temperature	Velocity constant
The sodium nitrosaminate spontaneously from the sodium diazoate.	4-Nitrodiazobenzene.....	13°	0.53
	4-Nitrodiazobenzene.....	10°	0.25
	2-Methyl-4-nitrodiazobenzene.....	10°	0.12
	2-Nitrodiazobenzene.....	10°	0.057
The diazonitrosaminate spontaneously from the diazodiazoate.	4-Nitrodiazobenzene.....	10°	0.32
	2-Methyl-4-nitrodiazobenzene.....	10°	0.12
	2-Methoxy-4-nitrodiazobenzene.....	10°	0.51
	2-Nitrodiazobenzene.....	10°	0.12
	4-Sulfodiazobenzene	5°	0.032
The diazonitrosaminate spontaneously from the nitrosamino acid	4-Nitrodiazobenzene.....	13°	0.19
	2-Methyl-4-nitrodiazobenzene.....	15°	0.2
	2-Methoxy-4-nitrodiazobenzene.....	15°	2.1
	2-Nitrodiazobenzene.....	10°	0.78
	4-Sulfodiazobenzene.....	5	0.07
The diazonium chloride from the nitrosamino acid by the action of HCl at a pH of 5.6.	4-Nitrodiazobenzene.....	15°	0.069
	2-Methyl-4-nitrodiazobenzene.....	15°	0.074
	2-Methoxy-4-nitrodiazobenzene.....	15°	0.13
	2-Nitrodiazobenzene.....	15°	0.54

The velocity constants of these changes of nitro- and sulfodiazobenzenes, computed graphically from experimental data (from the tangent of the straight-line slopes), are listed in the table above.

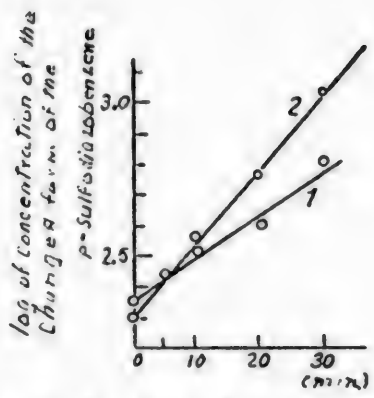


Fig. 5. Rate of spontaneous changes of the diazodiazoate (1) and the nitrosamino acid (2) into the diazonitrosaminate at 5°.

SUMMARY

1. The increase in the proportion of diazonium structure in an acid medium, of diazo structure in a neutral medium, and of nitrosamino structure in an alkaline medium is governed by Le Chatelier's law.

2. The spontaneous conversion of the sodium diazoate into the sodium nitrosaminate is an example of the change of a salt of a weak acid into the salt of a stronger acid and is a first order reaction.

3. The spontaneous change of a nitrosamino acid into a diazonitrosaminate is an example of change of one acid into another, less dissociated acid. The presence of amphoteric properties in the diazohydrate is due to the formation of a salt from the cation of the diazo compound and the anion of the nitrosamino acid. This is a first order reaction, since its velocity is governed solely by the rate of change of the nitrosamino acid into the diazotic acid.

4. The conversions of diazonitrosaminates or nitrosamino acids into diazonium chlorides, which take place under the action of hydrochloric acid, are pseudomonomolecular reactions, since the protons required for these conversions are taken, in part or wholly, from the external medium.

5. The reciprocal conversions of p-sulfodiazobenzene do not differ in principle from similar conversions of other diazo compounds, such as the nitrodiazobenzenes.

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THE PROBLEM OF SYNTHESIZING TERTIARY ALCOHOLS FROM CAMPHOR. I

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Until very recently individual ketones, including those of camphor, have found very limited employment in the Grignard synthesis of tertiary alcohols. This is due to the singular behavior of camphor in Grignard reactions and to the comparatively unexplored state of this field, as is shown by the literature references cited below.

Methyl borneol, the first representative of camphor tertiary alcohols, was synthesized by N.D.Zelinsky [1] and described as a substance with a m.p. of 154-156°. Owing to the difficulty of isolating tertiary methyl borneol, Wallach and Weinhaus [2], as well as I. Bredt and his associates [3], dehydrated the crude product of the reaction of camphor with CH_3MgI and converted directly to homocamphene. In addition, the latter authors have described their synthesis of tertiary phenyl and alpha naphthyl borneols.

Later, S.S.Nametkin and M.A.Shlezinger [4], in synthesizing methyl borneol, observed the generation of methane in abundance as the result of the enolization of camphor, reducing the yield of the normal reaction product. The methyl borneol was isolated from the 75-80% of unchanged camphor by binding the latter as a semicarbazone. S.S.Nametkin, A.S.Kichkina, and D.I.Kursanov [5] also reported the synthesis of tertiary phenyl borneol with a yield that was 20-30% of the theoretical, and pointed out that these low yields were also due to the formation of diphenyl as a by-product, and not only to the enolization of the camphor.

Recently, S.S.Nametkin and A.I.Shavrygin [6] have attempted to synthesize propyl borneol by reacting C_3H_7MgBr with camphor, but they recovered borneol, the product of reducing camphor, instead of the tertiary alcohol.

This research pointed to another reason for the abnormal trend of the Grignard reaction with camphor when AlkMgHal were used, where Alk = C_3H_7, etc., involving the reducing action of Grignard reagents.

On the other hand, M. Khoin [7], noting the capricious nature of the reaction, synthesized tertiary allyl borneol with a yield of nearly 100% by reacting camphor with allyl iodide and magnesium.

To synthesize tertiary propyl borneol, S.S.Nametkin and A.I.Shavrygin were forced to choose a detour. They first synthesized allyl borneol by Khoin's method, with the sole difference that they used allyl bromide instead of allyl iodide, thus obtaining higher and more constant yields. The allyl borneol was then readily converted into propylborneol by hydrogenation.

These data indicate that of the alkyl borneols that might be directly synthesized by a Grignard reaction, only methyl borneol is known, with only allyl borneol known among the allyl borneols, and phenyl borneol and alpha naphthyl borneol among the aryl borneols, while exact prescriptions for synthesis are available only for allyl borneol.

The occasion for our investigation of the Grignard reaction as applied to camphor was the inconsistency between the degree of enolization of the various ketones and their ability to form tertiary alcohols in the Grignard reaction.

Thus, according to the research of Bredt and Savelsberg [8], camphor in an ether solution is 29% enolized by CH_3MgI in 25 hours. According to Grignard and Blanchon [9], more strongly enolizing agents, such as iso-C_3H_7MgBr, enolize cyclohexanone by 40%, whereas mesityl oxide effects 56% enolization; correspondingly, 4-methylcyclohexanone is 46% enolized by tertiary C_4H_9MgCl, and 60% by mesityl oxide.

According to N D.Zelinsky [1], reacting cyclohexanone with CH_3MgI yields 66.6% of the theoretical quantity of methylcyclohexanone; 1-methylcyclohexanone-3 and CH_3MgI produce 1,3-dimethylcyclohexanone-3 with a 90% yield; the same substance with C_3H_7MgI yields 41.9% of 1-methyl-3-propylcyclohexanone-3; and, finally, the same substance with iso-C_3H_7MgBr yields 1-methyl-3-isopropylcyclohexanone-3, with a lower yield, to be sure.

Grignard and Blanchon have shown that at 40° cyclohexanone yields isopropylcyclohexanone-3, in addition to the enol, when reacted with iso-C_3H_7MgBr.

Lastly, according to V.I.Yesafov, mesityl oxide yields 50.9% of 2,4-dimethylhexadiene-2,4 when reacted with C_2H_5MgBr [10], 32.9% of a mixture of hendecadienes when reacted with iso-$C_5H_{11}MgBr$ [11], and 38.4% of 2,4-dimethylpentadiene-1,3 when reacted with CH_3MgI [12].

Bearing in mind the fact that the diene hydrocarbons were synthesized by the dehydration of the normal products of the Grignard reaction, i.e., α, β- unsaturated tertiary alcohols, involving appreciable losses of the latter, we should expect that the alcohol yields were actually much higher than the yields of the respective diene hydrocarbons.

Comparison of the foregoing data on the degree of enolization of the ketones indicates that camphor is not outstanding among them, and, in view of its behavior in the Grignard reaction, one of two alternatives is true: either the Bredt-Savelsberg figures are wrong or there is still another factor responsible for lowering the yields of tertiary alkyl borneols.

Among the other factors that hamper the normal course of the Grignard reaction, mention must be made of the reducing action of Grignard reagents, which has been pointed out by Grignard himself [13], as well as by M.I.Konovalov [14], Z. Iotsich [15], and many others.

But this factor does not operate in the reaction of camphor with CH_3MgI, and only experiment can provide the answer to the question posed above.

Though enolization of the camphor is the principle factor that lowers the yield of methyl borneol when camphor is reacted with CH_3MgI at 110° and 16°, the responsible factor at -15° is the formation of a molecular compound containing camphor. A similar product is partially formed in 16° experiments as well.

Since these molecular compounds do not evolve methane when decomposed with water or dilute acids, they are not at all related to the coordination compounds constructed in accordance with the views of Hess [16], Meisenheimer [17], and Terentyev [18]. Most likely, they are similar to the molecular compounds of aldehydes and ketones with incomplete Mg alcoholates of the $R - O - MgHal(R_1COH)_x$ type, where $x = 1$ or 2, and the $R - O - MgHalR_1CO - R_1$ type, investigated in detail by V.M.Tolstopyatov [19].

We were thus able to discover another factor that reduced the yields of tertiary methyl borneol, involving the reaction of camphor with the products of its own reaction with CH_3MgI, giving rise to fairly stable molecular compounds, constructed

most probably as specified by Tolstopyatov.

This hypothesis is borne out by the additional fact that the ether filtrate of the molecular compound contains a large quantity of the unreacted etherate of CH_3MgI.

Thus, when camphor is reacted with CH_3MgI at -15°, the resulting normal product – the etherate of methylmagnesium iodide borneolate – very quickly reacts with the unchanged camphor to form a coordination compound, which results, first, in diminishing the amount of camphor available for the synthesis and, second, in difficulties encountered in isolating the tertiary alcohols.

The material we have on the reaction at -15° also sheds light upon the reaction at +16°. The product with a lower percentage of magnesium and iodine doubtless contains a molecular compound of camphor; it is difficult, as yet, to say anything definite about it, since a mixture of the enolate and the carbinolate is present under these conditions. Hence, though the formation of a coordination compound is a parasitic reaction at low temperatures, this role is also assumed at higher temperatures by the enolization reaction, and, acting together, they end up by producing poor yields of methyl borneol.

In the synthesis of higher tertiary alkyl borneols still a third factor enters to lower the yields: the reducing action of AlkMgHal, which was referred to above and which has been confirmed by our experiments with C_2H_5MgBr.

EXPERIMENTAL

I. The Reaction of Camphor with CH_3MgI, Heated in a Toluene-Ether Solution

a) Methylmagnesium iodide was prepared with 2.4 Mg and 16 g of CH_3I in 50 ml of absolute ether. The excess ether, amounting to 26 ml, was driven off at 100° over an oil bath; then the bath temperature was raised to 110°, and a solution of 15.2 g of camphor in 50 ml of absolute toluene was poured into the reaction flask during the space of 20 minutes. The camphor used in these experiments was first recrystallized from alcohol and then carefully desiccated in a vacuum exsiccator over $CaCl_2$: it had a m.p. of 175° and its semicarbazone had a m.p. of 235°.

The reaction mass was kept at 110° while the camphor solution was added and for the next 100 minutes; the reaction was accompanied by the evolution of gas, 850 ml of which was collected at 13° and 726 mm, or 763.4 ml at 760 mm and 0°. The gas was collected over a saturated solution of sodium chloride, the first 500 ml of gas being released, the last 350 ml being used for analysis to determine its oxygen and C_nH_{2n} content. No unsaturated compounds were found in the gas; each 100 ml of which contained 0.73 ml of oxygen (mean of three determination); most of the gas consisted of methane. According to the amount of gas evolved, 34.0% of the camphor was enolized.

b) When the experiment was repeated, but with the camphor added over the course of an hour and a half, 1000 ml of gas was collected at 15° and 729 mm, equaling 893.2 ml at 0° and 760 mm. The degree of enolization of the camphor in this experiment was 39.8%.

The next day, a crystalline substance was found to have been formed in the reaction flasks; this substance was separated as quickly as possible from the liquid on a Schott filter, twice washed with ether, and placed in a vacuum exsiccator over H_2SO_4 for 2 hours. The resulting product was analyzed to determine its magnesium and iodine content. The analysis for magnesium was performed as follows: a weighed portion of the substance was boiled with 50 ml of 0.2 N HCl in a flask with a reflux condenser, the driven-off solid organic substance being collected within the condenser's inner tube. The magnesium was determined as $Mg_2P_2O_7$.

0.1828 g substance: 0.0593 g $Mg_2P_2O_7$.
0.3618 g substance: 0.1218 g $Mg_2P_2O_7$.
Found %: Mg 7.09; 7.36.
$C_{10}H_{15}OMgI$. Calculated %: Mg 8.05.
$C_{10}H_{15}OMgI(C_2H_5)_2O$. Calculated %: Mg 6.47.
$C_{11}H_{19}OMgI(C_2H_5)_2O$. Calculated %: Mg 6.21.

To determine the iodine, the substance was boiled with 50 ml of water, after which it was acidulated with dilute HNO_3 and precipitated with a solution of silver nitrate.

0.3234 g substance: 0.2164 g AgI.
0.1582 g substance: 0.1070 g AgI
Found %: I 36.33, 36.55.
$C_{10}H_{15}OMgI$. Calculated %: I 41.98.
$C_{10}H_{15}OMgI(C_2H_5)_2O$. Calculated %: I 33.73.
$C_{11}H_{19}OMgI(C_2H_5)_2O$. Calculated %: I 32.35.

Thus, the composition of the solid product is very close to that of an etherate of a magnesium iodide enolate of camphor, possibly with traces of the magnesium iodide enolate of camphor and the methylmagnesium iodide borneolate.

II. The Reaction of Camphor with CH_3MgI in Ether at 16°

In two experiments run at 16°, methylmagnesium iodide was prepared with 4.8 Mg and 30 g of CH_3MgI in 50 ml of ether. Over the space of 3 hours a solution of 30.4 g of camphor in 75 ml of ether was added to the resultant Grignard reagent. As the camphor was added, gas was seen to evolve, 1400 ml at 15° and 729 mm being collected within 3 hours, equaling 1250.5 ml at 0° and 760 mm. Thus, 27.9% of the camphor was enolized in three hours. The reaction mass continued to produce gas even after it was set aside to stand – an additional 1100 ml of gas at 14.5° and 736 mm, or 994.1 ml at 0° and 760 mm, was collected during 18 hours. Hence, the percentage of enolization rose to 50.08% for 21 hours.

The next day transparent crystals were found on the walls of the flasks; they were removed by decanting the liquid, washed several times with absolute ether and, quickly pressed between filter paper, placed for 2 hours in a vacuum exsiccator over H_2SO_4 and then subjected to analysis.

0.2253 g substance: 0.0655 g $Mg_2P_2O_7$.
0.2772 g substance: 0.0756 g $Mg_2P_2O_7$.
Found %: Mg 6.36, 5.96.

0.7806 g substance: 0.4984 g AgI.
0.3778 g substance: 0.2383 g AgI.
Found %: I 34.09, 34.08.

The substance was decomposed by boiling with dilute mineral acids. The organic substance driven off was collected on a weighed filter and weighed again after having been dried in an exsiccator. The following results were obtained:

1) 0.7806 g of the substance yielded 0.3164 g of distilled substance, or 40.53%; 2) 0.2253 g of the substance yielded 0.0943 g of distilled substance, or 41.85%.
$[C_{10}H_{15}OMgI(C_2H_5)_2O]$, the etherate of the magnesium iodide enolate of camphor, ought to yield 40.41% of camphor upon decomposition.

The distilled substance had a m.p. of 174°; a test sample mixed with camphor fused at 174.5°.

A large quantity of a crystalline substance soon began to separate out from the decanted liquid; this separated substance was then washed three times with

ether, transferred to a Schott filter, and – after standing for 2 hours in an exsiccator over H_2SO_4 – analyzed.

0.5272 g substance: 0.1277 g $Mg_2P_2O_7$.
Found %: Mg 5.29.
0.2545 g substance: 0.1346 g AgI.
0.3239 g substance: 0.1716 g AgI.
Found %: I 28.58, 28.63.

III. Reaction of Camphor with CH_3MgI in Ether at -15°

In six experiments, 2.4 Mg, poured into 20 ml of absolute ether, was reacted with 15 g of CH_3I in ether (1:1); after preparation, the Grignard agent was chilled to -15°, and then a solution of 15.2 g of camphor in 30 ml of ether was added during 2 hours, with constant stirring. The reaction is accompanied by the slight evolution of gas; in one of the experiments we collected 250 ml at 12° and 736 mm, or 228.5 ml at 0° and 760 mm. Computing the enolization of camphor from the maximum quantity of gas, we find it equals 10.2%. In most of the experiments, crystallization set in immediately after camphor was added. The resultant products were decanted from theether solution, transferred to a Schott filter, washed three times with absolute ether, and analyzed after having stood in an exsiccator over H_2SO_4. No gas is evolved when the product is decomposed by water or by dilute acids.

When heated over an open flame, the product fused with decomposition and yields a sublimate, from which camphor, with a m.p. of 174° after recrystallization from alcohol, is obtained.

0.9296 g substance: 0.1780 g $Mg_2P_2O_7$.
1.2721 g substance: 0.2354 g $Mg_2P_2O_7$.
Found %: Mg 4.18, 4.05.

0.6332 g substance: 0.3138 g AgI.
Found %: I 26.78.
$C_{10}H_{16}OC_{11}H_{19}OMgI$. Calculated %: Mg 5.16; I 26.95.
$(C_{10}H_{16}O)_2MgI_2$. Calculated %: Mg 4.17; I 43.58.

In one of the experiments, after the ethereal liquid had been decanted, the product was treated three times with absolute ether before analysis, being boiled each time for one hour. The product, thus treated, exhibited the following results upon analysis:

0.6587 g substance: 0.1260 g $Mg_2P_2O_7$.
0.5528 g substance: 0.1060 g $Mg_2P_2O_7$.
Found %: Mg 4.17, 4.18.

0.6833 g substance: 0.3334 g AgI.
Found %: I 26.36.

It should be borne in mind, however, that the composition of the products obtained in the experiments at -15° is not constant; according to several analyses, the magnesium content of these products varies from 3.3 to 4.23%, with the iodine content ranging from 26 to 3.245%.

The decanted ethereal solution still contains a considerable quantity of the free etherate of CH_3MgI. Thus, an average of 116 ml of gas, measured at 14° and 745 mm, or 107.79 ml at 0° and 760 mm, has been recovered by decomposing 5 ml samples with water immediately after the complex product has been crystallized. Hence, each 5 ml of the ethereal liquid contained 0.8003 g of CH_3MgI.

The analytical data for the crystalline product enable us to consider its composition as basically that of a molecular compound of camphor with methylmagnesium iodide borneolate.

IV. The Reaction of Camphor with C_2H_5MgBr, Heated in a Toluene-Ether Solution

Ethylmagnesium bromide was prepared with 2.4 g of Mg, and 12 g of C_2H_5Br in 50 ml of absolute ether. The 24 ml excess of ether was driven off at 100° over an oil bath, after which the temperature was raised to 110°, and 15.2 g of camphor dissolved in absolute toluene was then added to the reaction flask over a course of 30 minutes. The reaction was accompanied by the evolution of gas, which was collected in a gasometer over a saturated solution of NaCl. We collected 1.8 liters of gas on the average (of five experiments), measured at 19° and 746 mm, or 161.6 ml at 0° and 760 mm.

Analysis of the gas indicated that each 100 ml contained 37.9 ml of ethylene and 8.4 ml of oxygen; whence the nitrogen totaled 31.5 ml. In view of the fact that the residue of 22.2 ml of the gas consists of ethane, the percentage of enol in the camphor is 17.83%. The degree of reduction of the camphor is 27.3%, computed from the yield of ethylene upon the condition that the ethylene is not the product of disproportionation: $2C_2H_5 \rightarrow C_2H_4 + C_2H_6$, but that the C_2H_5 decomposes into ethylene and hydrogen, which is used in reducing the camphor. Thus, in this short interval of time, an average of 45% of camphor is used up in by-products.

The next day a crystalline substance was found to have been formed in the reaction flask; this substance was separated out as rapidly as possible on a Schott filter, washed twice with absolute ether, and dried for 24 hours over H_2SO_4 in a vacuum exsiccator.

0.2100 g substance: 0.0709 g $Mg_2P_2O_7$.
0.2172 g substance: 0.0790 g $Mg_2P_2O_7$.
Found %: Mg 8.31, 8.02.
0.2136 g substance: 0.1221 g AgBr.
0.2234 g substance: 0.1272 g AgBr.
Found %: Br 24.52, 24.24.

When the analysis was repeated with products of other experiments, the following results were obtained.

0.2102 g substance: 0.0746 g $Mg_2P_2O_7$.
0.2062 g substance: 0.0723 g $Mg_2P_2O_7$.
Found %: Mg 7.76, 7.71.

0.2003 g substance: 0.1120 g AgBr.
0.2062 g substance: 0.1217 g AgBr.
Found %: Br 23.78, 25.11.

$C_{10}H_{15}OMgBr$. Calculated %: Mg 9.53; Br 31.30.
$C_{10}H_{15}OMgBr(C_2H_5)_2O$. Calculated %: Mg 7.39; Br 24.25.
$C_{10}H_{17}OMgBr(C_2H_5)_2O$. Calculated %: Mg 7.34; Br 24.12.
$C_{12}H_{21}OMgBr(C_2H_5)_2O$. Calculated %: Mg 6.77; Br 22.23.

According to the analysis data, the product is closest in composition to the etherate of the magnesium bromide enolate of camphor and to magnesium bromide borneolate.

The organic mass produced when this product was decomposed with water was tested by the Haller method to determine whether it contained borneol. The result was positive. Borneol, with a m.p. of 202°, was isolated by saponification with a succinic acid ester.

SUMMARY

1. It has been shown that when camphor is reacted with CH_3MgI at high temperatures, the chief reason for the low yield of the tertiary methyl borneol is enolization of the camphor.

2. It has been shown that when the same reaction is performed at 16°, the enolization of the camphor is accompanied by the formation of a coordination compound that contains camphor. When the reaction is carried out at -15°, the latter reaction is the principal factor responsible for the low yield of the tertiary methyl borneol.

3. It has been shown that when camphor is reacted with C_2H_5MgBr and heated, the predominant side reaction is the reduction of camphor to borneol.

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* See CB translation p. 1055 ff.

THE SYNTHESIS OF 2,3,5,6-TETRAMETHYLPYRIDINE

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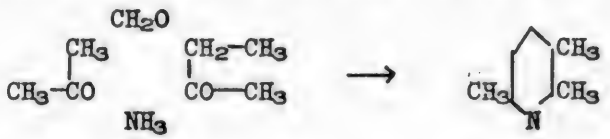
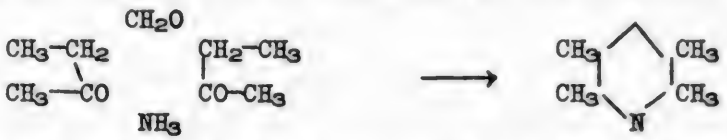
In a paper on the synthesis of 3,5-dimethylpyridine and 2,3,5-trimethylpyridine [1] we reported that when methyl iodide was reacted with 3,5-dimethylpyridine, a small quantity – about 0.3 g – of a base was recovered as a by-product, with a composition of $C_9H_{13}N$ according to the results of analysis (picrate m.p. = 173°, chloroplatinate m.p. = 174°, and aurate m.p. 174°). The method of synthesizing this base led us to assign it the structure of 2,3,5,6-tetramethylpyridine, as the methyl groups usually occupy the 2 and 6 positions in a Ladenburg reaction. But since not enough of the base had been synthesized, its structure was not confirmed by other reactions.

The same base, as a picrate with a m.p. of 172-173°, was likewise isolated as a by-product in the condensation of a mixture of one molecule of formaldehyde, one molecule of acetone, and one molecule of methyl ethyl ketone with ammonia in the presence of a catalyst – alumina. It was identified by its picrate [2]. The principal product obtained in this reaction was 2,3,6-trimethylpyridine:



2,3,5,6-Tetramethylpyridine could be synthesized if two molecules of methyl ethyl ketone and one molecule of formaldehyde were condensed with ammonia:



This was confirmed by the results of the present investigation. When a mixture of formaldehyde and methyl ethyl ketone in the cited proportions is condensed in the presence of alumina as a catalyst under the conditions described earlier [2], the principal reaction product was 2,3,5,6-tetramethylpyridine. No tetramethylpyridine with such a symmetrical arrangement of the methyl groups has been known hitherto.

It is easily isolated from a mixture of bases as an easily crystallizing picrate with a m.p. of 173-173.5°, found to be as identical with the product previously prepared by the Ladenburg reaction. The arrangement of the methyl groups was established from the products synthesized in oxidation with permanganate. We synthesized an acid $C_9H_9NO_4$, with a m.p. of 238°, which turned orange with $FeSO_4$ and yielded 2,5-dimethylpyridine when distilled with lime. When this acid is heated to 185-190°, carbon dioxide is liberated, giving rise to 2,5-dimethyl-3-carboxylic acid, which we previously synthesized by oxidizing the base 2,3,5-trimethylpyridine, isolated from bituminous-coal tar [3] and synthesized by condensing propionic and

acetic aldehydes with ammonia.

Another oxidation product was an acid with the same composition, and with a m.p. of approx. 308°. This acid did not turn orange with $FeSO_4$; distilling it with 2,6-dimethylpyridine yielded 2,6-dimethylpyridine, identified as the picrate. This proved the structure of the acid to be 2,6-dimethylpyridine-3,5-dicarboxylic acid. An acid of this structure is known [4], but the melting point is given as somewhat higher: 315° and 315-320°, which may be due to a difference in the temperature of heating.

The cited data seem to prove that the structure of the compound is 2,3,5,6-tetramethylpyridine.

Of the homologs of pyridine with saturated side chains, this base is interesting because of the fact that it is a solid - prisms with a m.p. of 81-82° (the m.p. was earlier given as 71-72° for the product synthesized by the Ladenburg reaction), which sublime at ordinary temperature. The b.p. is 197-198° (by stub thermometer). The odor of the base is somewhat like that of 2,6-dimethylpyridine: peppermint. The corresponding homologs of pyridine are liquids and are not volatile at ordinary temperature.

These physical properties are very much like those of symmetrical 1,2,4,5-tetramethylbenzene: m.p. 79-80°, subliming at room temperature, and with a camphor odor. Nor are these physical properties usually encountered in the corresponding homologues of benzene.

EXPERIMENTAL

2,3,5,6-Tetramethylpyridine. A mixture of 300 g of methyl ethyl ketone and 200 g of 30% formalin was passed drop by drop over a catalyst - alumina - placed in a copper tube 70 cm long and 2 cm in diameter and heated to 340-350° at a rate of approximately 50 g per hour. The alumina used was in the form of porous lumps [2]. A rapid stream of ammonia, used in excess, was passed through the tube at the same time, at the rate of about 300 ml per minute. The condensate was treated with hydrochloric acid, and the neutral products were separated out. The base was isolated from the acid solution by means of potash, then extracted with ether and washed with potash. Distillation with a dephlegmator yielded the following fractions: I - 100-165° (6 g); II - 165-185° (7 g); III - 185-205° (37 g); IV - 205-220° (10 g); and V - 220-260° (6 g).

Separation of the bases was effected by fractional precipitation with picric acid, followed by recrystallization of the picrates from alcohol. The first and second picric-acid precipitations of the 185-205° fraction, totaling one-third of the theoretical quantity, yielded 19 g of the same picrate, which fused at 173-173.5° after being twice recrystallized from alcohol.

7 g of the same picrate was recovered from the 205-220° and 165-185° fractions, with the same m.p. of 173-173.5°.

Another 4 g was recovered from the alcoholic mother liquors after recrystallization. The total recovered was 31 g, corresponding to 11.5 g of the base, or 4%, based on the methyl ethyl ketone used.

The base recovered from the picrate boiled at 197-198° (by stub thermometer) and fused at 81-82°. The substance sublimed at ordinary temperature.

The synthesis of 2,6-dimethylpyridine-3,5-dicarboxylic acid. For 1.5 g of the base, we took 14 g of permanganate (the theoretical quantity for oxidation to the tetracarboxylic acid). The base was added to a solution of 7 g of the permanganate in 200 ml of water. 20 minutes later, the solution was decolorized, and then

the other 7 g of permanganate was added; the solution did not decolorize completely during 24 hours of heating over a bath. Decolorized by the addition of alcohol and with the manganese dioxide filtered out, the solution was evaporated to dryness, diluted with 5 ml of water, and precipitated with copper acetate while heated. A small quantity of a sky-blue precipitate of the copper salt settled out; it was decomposed with hydrogen sulfide. After the copper sulfate had been removed, the acid solution was evaporated to dryness. The residue did not fuse when heated to 335°; it turned $FeSO_4$ red. Heating it with lime yielded pyridine, which was identified by its picrate. A small quantity of ash was left after combustion; the acid was therefore converted into a silver salt. Determination of the silver in the silver salt, dried at 120°, yielded a percentage that was 1% less than the amount required for the tetracarboxylic acid.

0.3420 g substance: 0.2826 g AgCl.
Found %: Ag 62.1
$C_9HO_8NAg_4$. Calculated %: Ag 63.1.

Titration of the acid, isolated from the silver salt in the usual way and dried at 120°, yielded:

0.1036 g substance: 14.9 ml 0.1 N NaOH.
Found %: equivalent – 69.5.
$C_9H_5O_8N$. Calculated %: equivalent – 63.8.

These figures indicate that the acid was not a pure tetracarboxylic acid.

When the acid was heated in a small test tube fitted with a branch pipe immersed in baryta water, carbonic acid began to be evolved at 150°, CO_2 generation stopping at 180-190°. The residue was dissolved in dilute hydrochloric acid and evaporated several times, with water added each time, to remove the hydrochloric acid, which yielded a small quantity of an acid that was soluble with difficulty, did not color $FeSO_4$, and had a m.p. of 308-309°; the initial tetracarboxylic acid was readily soluble.

In our next experiment, we took 6 g of permanganate in 200 ml of water and added 2.5 g of the base to the hot solution. Ten minutes after the solution was decolorized we added another 6 g of permanganate – the theoretical quantity required to oxidize the base to a dimethyldicarboyxlic acid. The solution was decolorized by 1 hour of heating over a bath. The solution, with the manganese dioxide filtered out, was evaporated to a volume of 5 ml, hydrochloric acid was added, and the precipitate was separated on a suction filter and washed twice with water (the wash water and the mother liquor were called No. 1). Desiccated at 125°, it fused at 258° with decomposition. Distillation with lime yielded 2,6-dimethylpyridine, identified as its picrate, with a m.p. of 161-162°; it yields a crystalline hydrochloride. To purify the acid with a m.p. of 258°, 0.8 g was recrystallized from water, and needles with a m.p. 307-308° settled out. The acid did not color $FeSO_4$, nor did it yield a copper-salt precipitate. More of the same crystals were recovered from the mother liquor.

Titration of the Acid, Desiccated at 125°.

0.0914 g substance: 9.4 ml 0.1 N NaOH.
Found : equivalent – 97.20.
$C_9H_9O_4N$. Calculated : equivalent – 97.50.

These figures indicate that the acid with a m.p. of 307-308° is 2,6-dimethylpyridine-3,5-dicarboxylic acid.

The mother liquor, called No. 1, was acidulated with hydrochloric acid, and after evaporation and removal of the potassium-chloride precipitate on a suction fil-

filter, 0.3 g of a crystalline acid with a m.p. of 258° separated out upon standing; its properties and reactions indicate that it is identical with the 2,5-dimethylpyridine-3,6-dicarboxylic acid described below.

2,5-Dimethylpyridine-3,6-dicarboxylic acid. The quantity of permanganate sufficient only for oxidation to the dimethylcarboxylic acid was used. 4.7 g of $KmNO_4$ in 150 ml of water was taken for 1.6 g of the base, and another 2.9 g of permanganate was added after the solution had been decolorized. Oxidation was concluded in 30 minutes. The solution, with the manganese dioxide filtered out, was evaporated to 5 ml and thrown down with silver nitrate. The silver salt was decomposed with hydrogen sulfide, and the aqueous solution of the acid was evaporated to a volume of 3 ml. When chilled, a precipitate settled out that fused at about 228° with decomposition. Recrystallization from water, in which the acid dissolves with difficulty, yielded a crystalline powder with a m.p. of 238° with decomposition. The resulting acid colored $FeSO_4$ after its preliminary neutralization with bicarbonate. It did not form a copper-salt precipitate with copper acetate, neither in the cold nor when heated.

Titration of the Acid, Desiccated at 120°

0.0894 g substance: 9.16 ml 0.1 N NaOH
Found : equivalent 97.60.
$C_9H_9O_4N$. Calculated : equivalent 97.50.

After titration, the solution was evaporated somewhat, acidulated with nitric acid, and precipitated with silver nitrate. The resulting silver salt – an amorphous precipitate – was desiccated at 120°.

0.1458 g substance: 0.1012 g AgCl.
Found %: Ag 52.20.
$C_9H_7O_4NAg_2$. Calculated %: Ag 52.70.

After precipitation of the silver chloride, (no nitric acid was added), the hydrochloric solution was evaporated to dryness, diluted with water, and again evaporated until the odor of hydrochloric acid had vanished completely. The residue was distilled with lime. This yielded a base, whose picrate fused at 164-165° and exhibited no depression when mixed with the picrate of 2,5-dimethylpyridine synthesized by the Errera method [5]. The odor of the base remained the same.

0.119 g of the acid was heated in a small test tube to 180-195° until all the carbon dioxide had been removed. The residue in the test tube fused into a homogeneous mass, which solidified again upon cooling. The resulting substance dissolved readily in water, whereas the initial acid dissolved in water with difficulty. After dissolution, heating, and cooling, needles with a m.p. of 183-185° settled out, with properties that corresponded to those of 2,5-dimethylpyridine-3-carboxylic acid, previously synthesized by us by oxidizing the base 2,3,5-trimethylpyridine [1]; it exhibited no depression when fused in a mixed test sample with the latter. The acid did not color $FeSO_4$ and yielded a copper salt of a typical purple color. Distillation with lime yielded 2,5-dimethylpyridine, which was identified in its picrate.

These data enable us to establish the structure of the acid with a m.p. of 238° as 2,5-dimethylpyridine-3,6-dicarboxylic acid, not described in the literature.

SUMMARY

1. Symmetrical 2,3,5,6-tetramethylpyridine, not described in the literature, has been synthesized by condensing a mixture of methyl ethyl ketone (2 mols) and formaldehyde (1 mol) with ammonia in the presence of alumina as a catalyst. The

physical properties of the base: m.p. 81-82°, sublimes at room temperature, are unusual for the corresponding homologs of pyridine.

2. The structure of the base as 2,3,5,6-tetramethylpyridine has been established by synthesizing oxidation products – acids: 2,5-dimethylpyridine-3,6-dicarboxylic acid, 2,5-dimethylpyridine-3-carboxylic acid, and 2,6-dimethylpyridine-3,5-dicarboxylic acid.

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RESEARCH ON THE REACTION OF SULFUR WITH UNSATURATED COMPOUNDS

III. SYNTHESIS OF α-PHENYLTHIOPHENE

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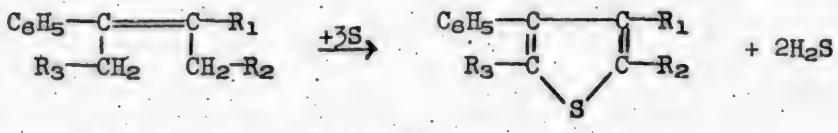
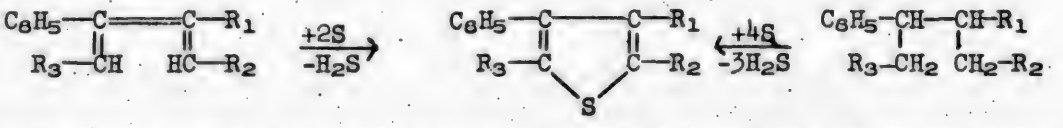
In our preceding reports [1-5] we showed that α,β-alkyl-substituted styrenes react with sulfur at 190-200°, forming β-phenylthiophene or its homologs, according to the diagram:

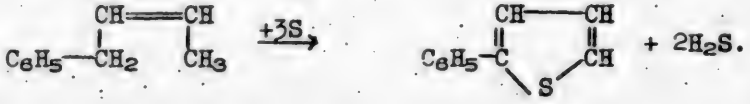


(R_1, R_2, R_3 = H, alkyl).

This method proved to be a new and convenient method of synthesizing β-phenylthiophene and its homologs. We also investigated the effect of the introduction of various substituents in the aromatic ring of the initial α,β-alkyl-substituted styrenes upon this reaction [2,5]. Lastly, we found that β-phenylthiophene or its homologs are also formed when sulfur acts upon the homologs of 2-phenylbutadiene-1,3 and 2-phenylbutane.

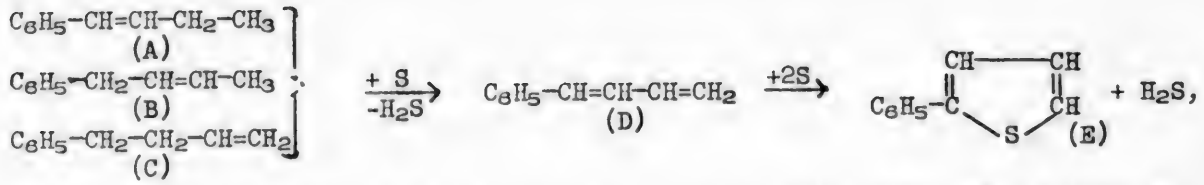


The present report deals with research on the feasibility of synthesizing α-phenylthiophene in the same way as was done with the beta isomer, i.e., by a diagram similar to the one cited above:



It was found, in agreement with our suppositions, that when 1-phenylbutene-2 is heated with sulfur at 190-200°, we get a yield of α-thiophene that is 15% of the theoretical. But, since this hydrocarbon is fairly inaccessible, we investigated the sulfuration of two other isomeric 1-phenylbutenes (Δ^1 and Δ^3) in order to work out a simple and convenient method of synthesizing α-phenylthiophene. In each case, we found that α-phenylthiophene was synthesized with a yield that was 35% or 25% of the theoretical, respectively. We thus demonstrated that α-phenylthiophene can by synthesized by the action of sulfur upon all the isomers of 1-phenylthiophene (A, B, and C), in accordance with:

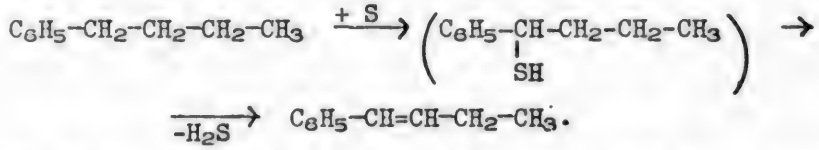
*Deceased.



irrespective of the location of the double bond in the side chain. The latter factor affects only the yield of α-phenylthiophene, which is a maximum (35%) when the double bond is closest to the aromatic ring (A).

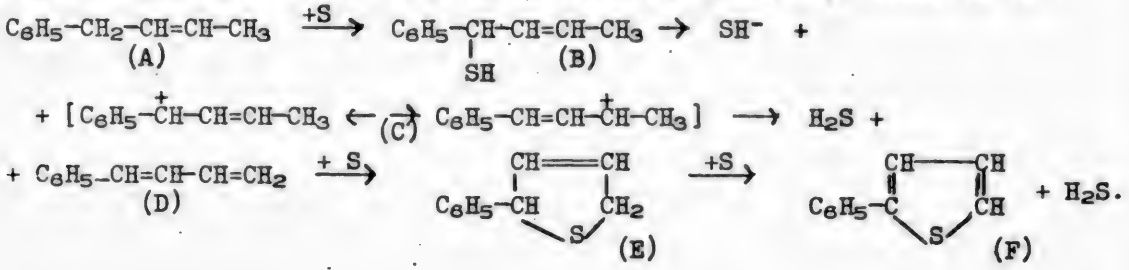
To confirm the feasibility of intermediate S-dehydrogenation of the initial 1-phenylbutene to 1-phenylbutadiene-1,3 (D), as indicated in the above diagram, we investigated the sulfuration of the latter. This reaction yielded 8.5% of the expected α-phenylthiophene. It must be assumed that the lower yield of the latter compound than was obtained in sulfurating the 1-phenylbutenes is due to the extremely pronounced tendency of 1-phenylbutadiene-1,3 to polymerize.

Finally, we have found that α-phenylthiophene is formed with a yield of about 5% by heating 1-phenylbutane with sulfur for a long time. We assume that this hydrocarbon is dehydrogenated by sulfur (1-phenylbutanethiol-1 being formed as an intermediate product) to 1-phenylbutene-1, which is then converted into α-phenylthiophene:



Thus, we have discovered a new way of synthesizing α-phenylthiophene. Up to recently, the latter compound has been synthesized only twice: by the action of phosphorus sulfides upon benzoylpropionic (or benzoylsuccinic) acid [6] or on its sodium salt [7], with a yield of 10 and 30%, respectively. The method of synthesizing α-phenylthiophene developed by us excels the foregoing methods considerably in point of its simplicity, the availability of the initial products, and the yield of the end product.

The data now available to us on the sulfuration of phenyl olefins [3], resulting in the formation of phenylthiophenes compel us to expand and change somewhat the hypothetical scheme of this reaction previously given [1]. When sulfur reacts with a phenyl olefin (1-phenylbutene-2 (A) in the most complex case), a free-radical reaction of S-oxidation takes place, affecting the methylene group located at the alpha position to the double bond. This reaction is broken off at the formation of an α,β-unsaturated mercaptan (B). Its further decomposition may be pictured as an ionic reaction of eliminating hydrogen sulfide (the E_1 type). The detachment of the sulfhydryl group during this reaction results in the formation of a carbonium ion (C) representing two resonating structures (without allowing for structures in which the bonds of the aromatic ring take part). Then a proton is detached, and the particle is stabilized as a phenyl-1,3-diolefin (D):



The latter (D) reacting with sulfur, apparently is converted into phenyldihydrothiophene (E) which is dehydrogenated at the instant of its formation into phenylthiophene (F). Nor may we exclude the possibility of the preliminary isomerizing of the initial phenyl olefin, the double bond being shifted from the side chain to the aromatic ring, into the respective styrene, which in turn reacts with sulfur as in the diagram cited above. Such isomerization of the phenyl olefins takes place very readily, as we know [8,9].

In the sulfuration of the phenyl olefins we have observed their simultaneous partial reduction by the generated hydrogen sulfide. For example, when sulfur is reacted with 1-phenylbutene-1, we get 6.5% of 1-phenylbutane:

$$C_6H_5-CH=CH-CH_2-CH_3 \xrightarrow{+H_2S} C_6H_5-CH_2-CH_2-CH_2-CH_3 + S,$$

in addition to the α-phenylthiophene. When the reaction mixture was distilled, in our experiment with 1-phenylbutene-3, we recovered a negligible quantity of toluene. Its formation is apparently due to the decomposition of the sulfuration products and indicates the shift of the double bond to the aromatic ring. The mechanism of this reaction is not altogether clear; the literature contains a reference [10] to a similar case, in which toluene is formed when stilbene is sulfurized:

$$C_6H_5-CH=CH-C_6H_5 \xrightarrow{+2H_2S} 2C_6H_5-CH_3 + 2S.$$

Our results enable us to conclude that the phenylthiophenes and their homologs are formed by the action of sulfur upon the phenyl-substituted olefins, phenylbutadiene and its homologs, and the higher alkyl derivatives of benzene. In all these instances, the thiophene ring is formed by closing the aliphatic radical through sulfur. This radical must, therefore, contain no less than four carbon atoms in the straight chain, independent of the presence or location of double bonds in the chain, the latter affecting only the yields of the phenylthiophenes. The yields of phenylthiophenes are a maximum in the homologs of styrene, but are lower than those of the corresponding phenyl mono-olefins in the case of the phenyldiolefins, and especially, the alkyl derivatives of benzene.

EXPERIMENTAL

Action of Sulfur upon 1-Phenylbutene-1

1-Phenylbutene-1 (β-ethylstyrene) was synthesized by dehydrating 1-phenylbutanol-1. The alcohol was synthesized from phenylmagnesium bromide and butyraldehyde and was dehydrated by phosphoric acid. The resulting hydrocarbon was desiccated over calcium chloride and repeatedly fractionated over metallic sodium. The yield of 1-phenylbutene-1, with a b.p. of 194.4-197.0° (755.4 mm), was 48% of the theoretical. The synthesized pure 1-phenylbutene-1 possessed the following constants:

B.p. 196.2° (755.4 mm).

d_4^{20} 0.8965; n_C^{20} 1.5273; n_D^{20} 1.5334; n_F^{20} 1.5478.

Parachor

γ^{20} 32.01: Found: P 350.8.
Calculated: P 352.1 (Segden method);
Calculated: P 352.8 (Memford and Phillips method).

Literature data on 1-phenylbutene-1: Levina and Shcheglova [9]: b.p. 65.5-66° (4 mm); d_4^{20} 0.9006; n_D^{20} 1.5378. Ward and Fulweiler [11]: b.p. 197.1°; d_4^{20} 0.8927; n_D^{20} 1.5249. Riiber [12]: b.p. 77° (10 mm); d_4^{20} 0.9106; n_D^{20} 1.5337.

In all instances of sulfurating the phenyl olefins, the reaction was carried

out under the conditions described in our previous reports [1-5]. 39.3 g (0.32 mol) of 1-phenylbutene-1 and 28.9 g (0.9 gram atom) of sulfur were heated to 200-250° for 15 hours until no more hydrogen sulfide was evolved. The resulting black tarry mass was fractionated in vacuum. Two broad fractions were collected: 2.6 g with a b.p. of 48-60° (3 mm); and 16.85 g with a b.p. of 80-105° (3 mm). The residue weighed 24.2 g.

The first fraction was repeatedly distilled at standard pressure over powdered iron and then over metallic sodium, after which its constants were as follows: b.p. 178-180° (760 mm); d_4^{20} 0.8642; n_D^{20} 1.4937; $n_F^{20} - n_C^{20}$ 0.0148; γ^{20} 29.45.

These constants are in good agreement with those for 1-phenylbutane, synthesized and described by us in our present research (cf below) The resulting 1-phenylbutane was identified as the sulfonamide, with a m.p. of 94-95°, which agrees with the literature data [13] for butylphenyl sulfonamide (m.p. 94.5-95°).

The second fraction consists of yellowish crystals (the yield of the crude reaction product was 35%); they were purified by repeated recrystallization from deeply chilled 85% alcohol. The substance is recovered as an oil from the undiluted alcohol, as from other solvents, with or without chilling. The yield of the pure substance was 30% of the theoretical. The substance consists of silver-white lamellar crystals, which are readily soluble in the usual organic solvents and possess an odor that resembles that of diphenyl. Its constants are as follows:

M.p. 34.0-34.5°; b.p. 256.1° (760 mm).*

d_4^{35} 1.1215; n_C^{35} 1.6228; n_D^{35} 1.6320; n_F^{35} 1.6553.

Found: MR_C 50.37; MR_D 50.96; MR_F 52.44.

$C_{10}H_8S$. Calculated: MR_C 49.03; MR_D 49.45; MR_F 50.37.

Parachor

γ^{35} 40.16. Found: P 359.6.
Calculated: P 361.8 (by Gibling).

0.0659 g substance: 17.80 g benzene: Δt 0.119°.
0.0453 g substance: 17.80 g benzene: Δt 0.081°.
Found: M 159.6; 161.8.
$C_{10}H_8S$. Calculated: M 160.23.

0.1396 g substance: 0.2041 g $BaSO_4$ (by Gasparini).
0.1195 g substance: 0.1706 g $BaSO_4$.
Found %: S 20.08, 19.63.
$C_{10}H_8S$. Calculated %: S 20.03.

The synthesized substance volatilizes with steam. It sublimes with difficulty. When reacted with isatinsulfuric acid, it exhibits the characteristic indophenin reaction: intense bluish-purple color. When reacted with concentrated sulfuric acid, it turns red, changing to orange when the acid is present in excess. It is thrown down by water unchanged from a sulfuric-acid solution. It produces a white precipitate of a mercury derivative when reacted with an aqueous solution of mercury acetate; when heated this precipitate decomposes without fusing. Treatment with an aqueous solution of mercuric chloride and sodium acetate produces a coordination compound, consisting of tiny white crystals with a m.p. of 235-236° (with decomposition) after recrystallization from an excess of boiling alcohol.

The foregoing analytical data, the determination of the molecular weight, the constants and the chemical properties of the synthesized substance, all indicate beyond doubt that it is pure α-phenylthiophene. The melting point of a-phenylthiophene determined by us does not quite agree with that cited in the literature, [6]. We believe, however, that our figures are more reliable, since the α-phenyl-

*Literature data for α-phenylthiophene: Kues and Paal [6]: m.p. 40-41°.

thiophene synthesized by us by other methods as well never fused at a temperature above 34.6°, as will be shown below. Moreover, the synthesized α-phenylthiophene was subjected to the most careful purification, repeated distillation and recrystallization, and was fully identified.

Action of Sulfur upon 1-Phenylbutene-3

1-Phenylbutene-3 was synthesized from benzylmagnesium chloride and allyl bromide. The resulting hydrocarbon was treated in the cold with metallic sodium, and, after the sodium had been removed, it was fractionated with a tower. The yield of the hydrocarbon, with a b.p. of 176-178° (763.5 mm), was 58.4% of the theoretical. Its constants were:

B.p. 177.5° (763.5 mm).

d_4^{20} 0.8834; n_C^{20} 1.50344; n_D^{20} 1.50792; n_F^{20} 1.51920.

Parachor

γ^{20} 30.19. Found: P 350.8.
Calculated: P 352.1 (by Segden); 352.8 (Memford and Phillips).

Literature data for 1-phenylbutene-3: Levina and Shcheglova[9]: B.p. 176-178° (753 mm); 62° (13 mm); 59° (7 mm); d_4^{20} 0.8915; n_D^{20} 1.5065. Riiber [12]: B.p. 64° (10 mm); d_4^{20} 0.8831; n_D^{20} 1.5059. Hurd and Bollmann [14]: B.p. 175-178°; n_D^{20} 1.5090.

24.6 g (0.2 mol) of 1-phenylbutene-3 and 19.3 g (0.6 gram atom) of sulfur were heated for four hours, with the temperature gradually raised from 200° to 270°, until no more hydrogen sulfide was evolved. The resulting black mass was fractionated at standard pressure. Two broad fractions were recovered: 10 g of a 105-290° fraction, and 2.8 g of a 290-335° fraction. The second fraction, which crystallized completely in the condenser tube, was driven off with partial decomposition and the liberation of hydrogen sulfide. Both fractions were separately dissolved in acetone and treated with metallic mercury to remove any free sulfur. After filtration and distillation of the solvent, both fractions were subjected to further purification. The first fraction was purified by recrystallization from deeply chilled 90% alcohol, after having been distilled in vacuum, during which the substance crystallized in the condenser tube. This yielded 3.2 g of the pure substance (the yield was 14.4% of the theoretical), with a m.p. of 33.5-34.5°; d_4^{35} 1.1212; n_D^{35} 1.6310. These constants coincided with those already cited for α-phenylthiophene.

0.2158 g substance: 17.60 g benzene: Δt 0.398°.
0.0658 g substance: 21.08 g benzene: Δt 0.100°.
Found: M 158.1, 160.1.
$C_{10}H_8S$. Calculated: M 160.23.

0.1423 g substance: 0.2023 g $BaSO_4$ (by Gasparini).
0.2906 g substance: 0.4059 g $BaSO_4$.
Found %: S 19.20, 19.25.
$C_{10}H_8S$. Calculated %: S 20.03.

A test sample of the synthesized substance mixed with pure α-phenylthiophene exhibited no depression.

The second fraction proved to be almost insoluble in the usual organic solvents. It was recrystallized a few times from a large quantity of carbon bisulfide, and then from carbon tetrachloride. This yielded a finely crystalline lemon-yellow substance, which fused with decomposition at 288.5-289° and did not exhibit an indophenin reaction.

The small quantity of the substance synthesized and the considerable difficulty involved in its purification prevented us from investigating it closer.

Efforts to determine its molecular weight were fruitless, owing to its insolubility in benzene and camphor. Efforts to obtain a quantitative determination of the sulfur were likewise unsuccessful, since the substance resisted oxidation by concentrated sulfuric acid and a chromium mixture.

In a second experiment, 1-phenylbutene-3 was heated with sulfur to 220-230° for eight hours until no more hydrogen sulfide was evolved. The reaction product was distilled in vacuum. A broad fraction with a b.p. of 114-126° (17 mm) was collected. Above 126° decomposition set in, white fumes being evolved. The residue was distilled at ordinary pressure. This yielded 1.7 g of a substance that distilled over at 95-115°, whose constants were as follows after redistillation over metallic sodium: B.p. 109-111.0° (760 mm); d_4^{20} 0.8676; n_D^{20} 1.4968; γ^{20} 28.61.

These figures agree with the literature data for toluene [15]: B.p. 110.65° (760 mm); d_4^{20} 0.8669; n_D^{20} 1.49685; γ^{20} 28.5. The toluene recovered was identified as dinitrotoluene with a m.p. of 70.5-71°.

The usual purification of the fraction with a b.p. of 117-126° (14 mm) yielded α-phenylthiophene, with a m.p. of 33.5-34.5°, and a small quantity of lemon-yellow crystals with a m.p. of 289° (with decomposition).

The optimum conditions for synthesizing α-phenylthiophene from 1-phenylbutene-3 proved to be as follows: 66.0 g (0.5 mol) of the hydrocarbon and 48.5 g (1.5 gram atom) of sulfur were heated together for 20 hours, the temperature being gradually raised from 220 to 250° toward the end of the reaction. The reaction product was distilled with steam. The distillate was extracted with chloroform. The α-phenylthiophene remaining after the solvent had been driven off from the desiccated extract was purified by recrystallization from dilute alcohol. The yield of crude product was 20.7 g (25.8%). The yield of pure α-phenylthiophene, with a m.p. of 34°, was 17.5 g, or 21.8%. The previously described lemon-yellow crystalline substance with a m.p. of 289.5°, was recovered from the residue in the distilling flask by extraction with boiling isoamyl alcohol.

Action of Sulfur upon 1-Phenylbutadiene-1,3.

1-Phenylbutadiene-1,3 was prepared by dehydrating 1-phenylbuten-1-ol-3. The alcohol was prepared from cinnamaldehyde, and an excess of methylmagnesium iodide, being partially dehydrated during this very reaction. The reaction product was decomposed with ice and 20% sulfuric acid. The ether extract was stabilized by the addition of 0.1 g of hydroquinone. After the ether had been driven off, the residue was fractionated in vacuum with a trace of iodine present. This effected the dehydration of the residual unchanged alcohol. The distillate was desiccated over calcium chloride and was then refractionated in vacuum. The yield of 1-phenylbutadiene-1,3, with a b.p. of 67-78° (a mixture of the cis and trans isomers), was 35% of the theoretical. Refractionation in vacuum yielded the two separate isomers, whose constants were found to be as follows: trans-1-phenylbutadiene-1,3:

B.p. 69.2° (4 mm); d_4^{20} 0.9338; n_D^{20} 1.60852.

Parachor

γ^{20} 36.21. Found: P 342.0.
Calculated: P 341.1 (Segden method); 341.8 (Memford and Phillips method).

Literature data for trans-1-phenylbutadiene-1,3: Muskat and Herrmann [16]: B.p. 76° (11 mm); n_D^{28} 1.5920;

•Contary to the statements in the literature [16,17], the 1-phenylbutadiene-1,3, synthesized by us in the presence of a stabilizer did not have a sharp, acrid odor, but a pleasant one.

Cis--1-phenylbutadiene-1,3:

B.p. 76.9° (3 mm); d_4^{20} 0.9334; n_D^{20} 1.60948.

Parachor

γ^{20} 36.15. Found: P 341.9
Calculated: P 341.1 (Segden method); 341.8 (Memford and Phillips method).

Literature data for cis-1-phenylbutadiene-1,3; Muskat and Herrmann [16]. B.p. 86° (11 mm); n_D^{28} 1.5950. Klages [17]: B.p. 90° (15 mm); d_4^{16} 0.9309; n_D^{16} 1.61283.

For the reaction we used 32.5 g (0.25 mol) of 1-phenylbutadiene-1,3 (we took a mixture of the two geometrical isomers) and 16.0 g (0.5 g-atom) of sulfur. The reaction mixture was heated slowly. When the temperature reached 190°, a violent reaction suddenly set in, the temperature spontaneously rising to 250°, and hydrogen sulfide being evolved abundantly. After the exothermic reaction was over, the mixture was heated for an hour at 225° until no more hydrogen sulfide was evolved. The reaction product, a black tarry mass, was distilled in vacuum. A wide fraction, with a b.p. of 100-120° (5 mm), was collected; it was dissolved in ether and treated with mercury. Further fractionation of the reaction product yielded 3.3 g of α-phenylthiophene, with a b.p. of 250-260°, representing a yield of the crude product that was 8.3% of the theoretical. Redistillation over iron powder yielded 2.8 g of pure α-phenylthiophene, with a b.p. of 254-256.5° (762 mm) and a m.p. of 33.8-34.4° (after recrystallization from alcohol). A test sample, mixed with the α-phenylthiophene synthesized from 1-phenylbutene-1, fused at 33.8-34.0°. In addition to the α-phenylthiophene, we recovered about 5 g of polymers of 1-phenylbutadiene-1,3, with boiling points above 300°, which were not investigated further.

Action of Sulfur upon 1-Phenylbutene-2

The 1-phenylbutene-2 was synthesized by reducing 1-phenylbutadiene-1,3, prepared as described above, with sodium in alcohol. The resulting 1-phenylbutene-2 was distilled over maleic anhydride, washed with alkali and water, and desiccated over calcium chloride to get rid of any traces of diene hydrocarbons, and purified by fractional distillation. The initial 1-phenylbutene-2 possessed the following constants:

B.p. 177-178° (758 mm).
d_4^{20} 0.8861; n_C^{20} 1.50328; n_D^{20} 1.50779; n_F^{20} 1.51901

Parachor

γ^{20} 30.48. Found: P 350.3.
Calculated: P 352.1 (Segden method); 352.8 (Memford and Phillips method).

Literature data for 1-phenylbutene-2: Klages [17]: B.p. 176-178°; d_4^{15} 0.8857; n_D^{15} 1.5109: Riiber [12]: B.p. 68° (10 mm); d_4^{20} 0.8831; n_D^{20} 1.5101. Andre [20]: B.p. 177-178° (754 mm); d_4^0 0.8891.

11.9 g (0.09 mol) of 1-phenylbutene-2 and 8.6 g (0.27 gram atom) of sulfur were heated together at 212-217° for six hours. The reaction product, a black tarry mass, was distilled in vacuum (7 mm). The distillate was dissolved in ether and treated with metallic mercury. Further fractionation of the reaction product over powdered iron yielded 2.1 g of crude α-phenylthiophene, with a b.p. of 248.3-250.8 (yield 15.3% of the theoretical). Double recrystallization from alcohol yielded a pure substance with a m.p of 33.5-34.5°, whose identity with α-phenylthiophene was proved by a mixed fusion sample.

Action of Sulfur upon 1-Phenylbutane

The 1-phenylbutane (n-butylbenzene) was synthesized by adding an equimolecular mixture of butyl bromide and bromobenzene to an excess of metallic sodium in boiling benzene. The reaction mixture was then boiled for another 8 hours. The resulting 1-phenylbutane (the yield was 50% of the theoretical) was twice fractionated into a tower over sodium, after which it possessed the following constants:

B.p. 181.2° (767.0 mm).

d_4^{20} 0.8597; n_C^{20} 1.48554; n_D^{20} 1.48998; n_F^{20} 1.49928.

Parachor

γ^{30} 29.10: Found: P 362.6.
Calculated: P 363.1 (Segden method); 365.4 (Memford and Phillips method).

Literature data for 1-phenylbutane: Hennion [18]: B.p. 79° (23 mm); d_4^{20} 0.8608; n_D^{20} 1.4900; Galpern [19]: n_C^{20} 1.48578; n_D^{20} 1.48973; n_F^{20} 1.49962.

We used for the reaction: 13.4 g (0.1 mol) of 1-phenylbutane and 9.6 g (0.3 gram atom) of sulfur. Thirty minutes after the reaction mixture began to boil, hydrogen sulfide began to be evolved. The reaction was continued for 35 hours at 195-200°. The reaction product, a black tarry mass, was extracted with boiling methanol. After treatment with metallic mercury, the alcohol was driven off, and the residue was fractionated. This yielded 0.61 g of crude α-phenylthiophene (the yield was 5.1%, based on the sulfur used), with a b.p. of 242-254° (736 mm). Double recrystallization from dilute alcohol yielded a pure substance in the form of silvery flakes, which melted at 34° and turned bluish purple with isatinsulfuric acid. The identity of the substance synthesized with α-phenylthiophene was proved by a mixed fusion sample.

SUMMARY

1. The reaction of sulfur with three isomeric 1-phenylbutenes, 1-phenylbutadiene-1,3, and 1-phenylbutane has been studied. It has been shown that all these hydrocarbons react with sulfur to form α-phenylthiophene.

2. A new, simple, and convenient method of synthesizing α-phenylthiophene has been developed.

3. A mechanism has been proposed for the reaction in which the phenylthiophenes are formed from aliphatic-aromatic hydrocarbons that have no less than four carbon atoms in a straight chain in the aliphatic radical.

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SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

VI. SULFONATION OF α,α'-SUBSTITUTED HOMOLOGS OF PYRROLE

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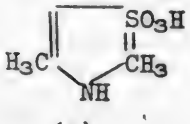
Continuing our research on the sulfonation of acidophobic compounds with pyridine sulfotrioxide [1], we have investigated the action of pyridine sulfotrioxide on α,α'-disubstituted pyrroles in order to synthesize a β-sulfo acid. In the literature, only one β-sulfo acid of the pyrrole series has been described. In 1935, Pratesi [2] synthesized 2,4-dimethyl-5-carbethoxypyrrolesulfonic-(3) acid by reacting chlorosulfonic acid with a solution of 2,4-dimethyl-5-carbethoxypyrrole in chloroform.

Our first efforts to sulfonate α,α'-disubstituted pyrroles under the conditions used in the synthesis of α-sulfo acids, i.e., heating a solution of pyrrole in dichloroethane for 10 hours at 100° with a triple excess of pyridine sulfotrioxide, did not produce the desired results: tarring was extremely heavy, and the reaction mixture could not be separated into its constituents. But, by changing the experimental conditions, we were able to effect sulfonation and to recover β-sulfo acids as barium salts. We effected the reaction in an ether or benzene solution, heating α,α'-disubstituted pyrrole in a sealed ampoule with pyridine sulfotrioxide to 100° for 5-6 hours. The reaction mixture was then treated in the cold with an aqueous suspension of barium carbonate. The next day the mass was evaporated to dryness over a water bath, and then extracted repeatedly with methanol. The residue left after the methanol extraction was treated again with a large quantity of hot water. The barium salts were precipitated from the methanol with ether. The aqueous extract was evaporated until the barium salts began to crystallize, settling out of the solution as white needles.

2,5-Dimethylpyrrole, 1,2,5-trimethylpyrrole, and 2,3,5-trimethylpyrrole were sulfonated. Sulfonation of 2,5-dimethyl- and 1,2,5-trimethylpyrrole resulted in the formation of β-mono- and β,β'-disulfo acids, as was proved by the analysis of their barium salts and oxidation products. The barium salts of the monosulfo acids are white crystalline substances, which are readily soluble in cold water and methanol; they are hydrolyzed by boiling with 15% hydrochloric acid, giving off sulfur dioxide. The barium salts of β,β'-disulfo acids are almost insoluble in cold water, somewhat more soluble in hot water, and insoluble in alcohol; they are also hydrolyzed by 15% hydrochloric acid, giving off sulfur dioxide.

It is worthy of note that sulfonation of the homologs of pyrrole with substituents at the α,α' positions yields disulfo as well as monosulfo acids. The formation of disulfo acids was similarly observed to occur in the case of sylvan, previously.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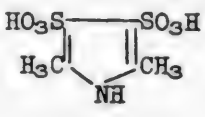
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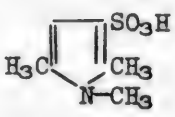
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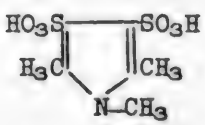
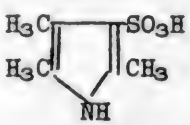

(IV)


(V)

1366 - 1367

EXPERIMENTAL

Sulfonation of 2,5-dimethylpyrrole. The 2,5-dimethylpyrrole was synthesized from acetonylacetone and ammonium carbonate by the Young and Allen method,[3].

B.p. 168.8-169° (767 mm); n_D^{20} 1.5070; d_4^{20} 0.9193; MR 30.93.

C_6H_9N Found. Calculated MR_D 30.38.

1 g of 2,5-dimethylpyrrole was heated in a sealed ampoule with 4.5 g of pyridine sulfotrioxide in ether solution to 100° for 5 hours. The reaction mixture was treated in the cold with an aqueous suspension of barium carbonate for 24 hours. Then the mass was evaporated to dryness over a water bath and extracted, first with alcohol, and then with hot water.

The 2,5-dimethylpyrrolesulfonic-(3) acid (I) was synthesized as the barium salt from the alcoholic extract by precipitation with ether. This yielded 1.1 g of the salt, representing a yield of 47%, based on the initial pyrrole. The salt is a white crystalline substance, which is readily soluble in water and alcohol, which decolorizes bromine water in the cold without isolating barium sulfate, and which is hydrolyzed by boiling with 15% hydrochloric acid, giving off sulfur dioxide.

3.182 mg substance: 1.383 mg $BaSO_4$.
3.535 mg substance: 1.561 mg $BaSO_4$.
Found %: Ba 25.58, 25.99.
$C_6H_8NSO_3Ba \cdot {}^1/_2H_2O$. Calculated %: Ba 26.29.

0.5 g of the salt was dissolved in a small quantity of concentrated sulfuric acid, and a mixture of chromic and sulfuric acid, with a slight excess (10%) of the oxidizing agent, was added to the solution. The spontaneous heating up of the mixture was controlled by water cooling; toward the end of the reaction the mixture was heated for 10 minutes over a water bath and set aside over night. The mixture was poured into water, and the acid solution was neutralized with baryta, the excess being precipitated with carbon-dioxide gas. After filtration, a product containing sulfur, nitrogen, barium, which decolorizes permanganate in the cold, was crystallized out of the evaporated solution.

4.112 mg substance: 2.902 mg $BaSO_4$.
3.821 mg substance: 2.701 mg $BaSO_4$.
Found %: Ba 41.53, 41.60.
$C_4H_3NO_6SBa$. Calculated %: Ba 41.39.

Its barium content indicates that the substance is the barium salt of a monosulfomaleamic acid, which confirms the entrance of the sulfo group into the 2,5-dimethylpyrrole at the β-position.

The 2,5-dimethylpyrroledisulfonic-(3,4) acid (II) was recovered as its barium salt from an aqueous extract of the sulfo mass. Evaporation caused the barium salt to crystallize out as white needles. This yielded 0.5 g, a yield of 11.6%, based on 2,5-dimethylpyrrole. The salt crystallizes with one molecule of water; it is poorly soluble in cold water, somewhat better soluble in hot water, and insoluble in alcohol; it decolorizes bromine water in the cold without evolving barium sulfate, while boiling it with 15% hydrochloric acid results in the generation of sulfur dioxide.

4.006 mg substance: 2.305 mg $BaSO_4$.
4.867 mg substance: 2.746 mg $BaSO_4$.
Found %: Ba 33.86, 33.20.
$C_6H_7NS_2O_6Ba \cdot H_2O$. Calculated %: Ba 33.62.

The barium salt was subjected to oxidation as above. This resulted in the isolation of a substance containing sulfur, nitrogen, and barium, which decolorizes a

permanganate solution in the cold.

2.376 mg substance: 1.766 mg $BaSO_4$.
5.936 mg substance: 4.369 mg $BaSO_4$.
Found %: Ba 43.74, 43.31.
$C_4H_2NS_2O_8 \cdot 1\frac{1}{2}$ Ba. Calculated %: Ba 43.04.

Its barium content indicated that the substance was barium disulfomaleamate, which shows that both of the sulfo groups actually occupy beta positions in the initial dimethylpyrrolesulfonic acid.

Sulfonation of 1,2,5-trimethylpyrrole. The 1,2,5-trimethylpyrrole was synthesized from acetonylacetone and an alcoholic solution of methyl amine.

B.p. 168-169° (766 mm); n_D^{20} 1.4992; d_4^{20} 1.4995; MR_D 34.92.

$C_7H_{11}N$. Calculated MR_D 35.33.

1 g of 1,2,5-trimethylpyrrole was heated for 8 hours in a sealed ampoule with 4.5 g of pyridine sulfotrioxide. The reaction mixture was treated as in the previous experiment.

The 1,2,5-trimethylpyrrolesulfonic-(3) acid (III) was prepared as 1 g of the barium salt, precipitated by ether from an alcoholic extract, representing a yield of about 40%, based on the initial pyrrole. The salt is readily soluble in water and alcohol, decolorizes bromine water, and is hydrolyzed by 15% hydrochloric acid, giving off sulfur dioxide.

5.550 mg substance: 2.271 mg $BaSO_4$.
17.377 mg substance: 7.008 mg $BaSO_4$.
Found %: Ba 24.08, 23.73.
$C_7H_{10}NSO_3Ba \cdot \frac{1}{2}H_2O$. Calculated %: Ba 23.42.

The salt was oxidized as before. This yielded a barium salt, whose barium content corresponded to the expected barium salt of the methyl amide of monosulfomaleamic acid.

7.434 mg substance: 5.054 mg $BaSO_4$.
1.956 mg substance: 2.016 mg $BaSO_4$.
Found %: Ba 40.01, 40.13.
$C_5H_5NSO_6Ba$. Calculated %: Ba 39.71.

The 1,2,5-trimethylpyrroledisulfonic-(3,4) acid (IV), was synthesized as the barium salt by evaporation of an aqueous extract. The salt crystallized as well-formed acicular white crystals. This yielded 0.5 g of the salt, i.e., some 12%, based on the 1,2,5-trimethylpyrrole used. Treatment of a salt solution with bromine water causes decolorization without the formation of a barium-sulfate precipitate. Hydrolysis is effected by boiling with 15% hydrochloric acid, giving off sulfur dioxide.

9.784 mg substance: 5.438 mg $BaSO_4$.
3.583 mg substance: 1.983 mg $BaSO_4$.
Found %: Ba 32.71, 32.55.
$C_7H_9NS_2O_8Ba \cdot H_2O$. Calculated %: Ba 32.46.

The barium salt was oxidized by a chromic-acid mixture as in the previous instance. A water-soluble product containing sulfur, nitrogen, and barium and decolorizing permanganate was recovered after neutralization of the reaction mixture with baryta. Its barium content corresponded to that of the expected barium salt of the methyl amide of disulfomaleic acid.

8.972 mg substance: 6.509 mg $BaSO_4$.
2.676 mg substance: 1.905 mg $BaSO_4$.
Found %: 41.69, 41.90.
$C_5H_4NS_2O_3 \cdot 1\frac{1}{2}Ba$, Calculated %: Ba 41.73.

2,3,5-Trimethylpyrrolesulfonic-(4) acid (V). The 2,3,5-trimethylpyrrole was synthesized from 2,3,5-trimethyl-4-carbethoxypyrrole by the Hess-Wissing method [4].

B.p. 178-179° (at 753 mm); n_D^{20} 1.4964; d_4^{20} 0.9219; MR_D 34.54.
$C_4H_{11}N$. Calculated MR_D 34.94.

1 g of 2,3,5-trimethylpyrrole dissolved in benzene was heated for 8 hours to 100° in a sealed ampoule with 4.5 g of pyridine sulfotrioxide. The reaction mixture was treated with a suspension of barium carbonate, and the pyridine was driven off with steam. The filtrate was evaporated to small volume, and the salt was precipitated with methanol. This yielded 0.6 g of the salt, or 25.4% in terms of the initial pyrrole. The salt is readily soluble in water, but insoluble in alcohol; it decolorizes bromine water, and it is hydrolyzed by 15% of hydrochloric acid, giving off sulfur dioxide.

2.864 mg substance: 1.301 mg $BaSO_4$.
2.837 mg substance: 1.304 mg $BaSO_4$.
Found %: Ba 26.73, 27.05.
$C_7H_{10}NSO_3 \cdot \frac{1}{2}Ba$. Calculated %: Ba 26.70.

SUMMARY

1. Three homologs of pyrrole with substituents in the α,α' positions have been sulfonated by means of pyridine sulfotrioxide.

2. The following acids have been isolated and described as their barium salts: 2,5-dimethylpyrrolesulfonic-(3) acid; 2,5-dimethylpyrrolesulfonic-(3,4) acid; 1,2,5-trimethylpyrrolesulfonic-(3) acid; 1,2,5-trimethylpyrroledisulfonic-(3,4) acid; and 2,3,5-trimethylpyrrolesulfonic-(4) acid.

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See CB translation p. 487 ff.

SYNTHESIS OF AMINOSULFONES

III. CONDENSATION OF ARYL AMINOSULFONES WITH ALDEHYDES

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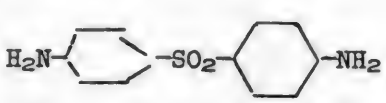
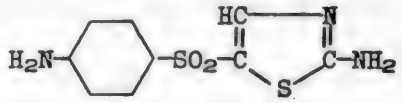
The reactivity of the arylaminosulfones differs but little from that of pure aromatic amines. This is apparently due to the slight influence of the sulfone group upon the amine. Like the purely aromatic amines, the aryl aminosulfones can condense with various kinds of aldehydes, with the formation of Schiff bases (anils).

Battle, Devine, and associates [1], basing themselves on the assertions of Gray and his co-workers [2] that the therapeutic activity of some sulfanilamide (streptocide) derivatives is not less than that of the streptocide itself, though their toxicity is lower, used diaminodiphenylsulfone to prepare a number of Schiff bases in which one or both of the amino groups was condensed with aromatic aldehydes. Some of these bases are listed in a British patent [3]. An American patent [4] speaks of the condensation products of 4-acylamino-4-aminodiphenylsulfone with aldehydes. A French patent speaks of the therapeutically active products synthesized by condensing 4,4'-diaminodiphenylsulfone with several aldehydes,[5].

Besides the condensation product of 4,4'-diaminodiphenylsulfones with salicylaldehyde, Callomon and Reiziss [6] investigated the therapeutic action of 4-(5-chloro-2-hydroxybenzylamino)-4'-aminodiphenylsulfone, but whereas the former product was of definite interest for chemotherapy, the latter was more toxic and less effective.

After our research had been completed, there was published a report by Jane and his associates [7] on their synthesis of a number of Schiff bases by condensing 4-nitro-4'-aminodiphenylsulfone with a number of aldehydes. In our chemotherapeutic study of the condensation products of aminosulfones with aldehydes, we picked 4,4'-diaminodiphenylsulfone (I) and 4-aminophenyl-2'-amino-thiazolyl-5'-sulfone (II), known as promizole [8] as the initial products for these condensations:





The following aldehydes were explored: butyraldehyde, heptanal, decanal, p-dimethylaminobenzaldehyde, cotarnine, vanillin, α-naphthaldehyde, and furfural.

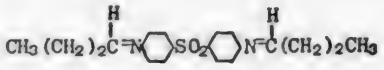
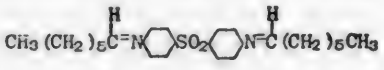
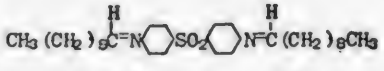
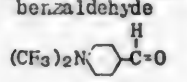
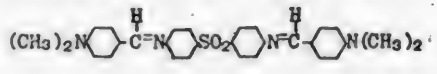
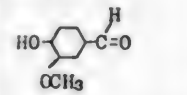
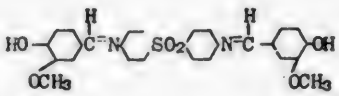
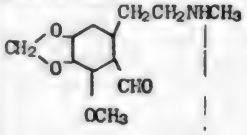
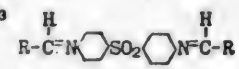
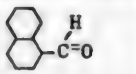
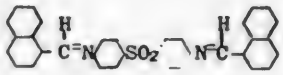
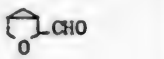
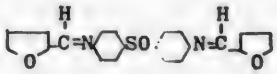
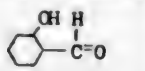
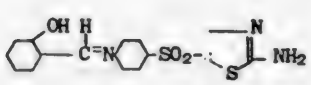
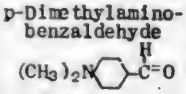
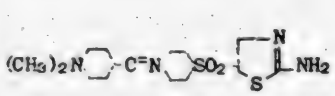
The condensation products (Schiff bases) have very low solubilities. It is impossible to refine them by recrystallization. Adequate purity is achieved by carefully washing them with organic solvents (methanol, ether, etc.). Most of the synthesized compounds do not have sharply defined melting points. We judged their purity by their elementary analyses.

EXPERIMENTAL

General Methods

The diaminodiphenylsulfone and the aldehyde, taken in stoichiometrical proportions or with a slight excess of the aldehyde, were stirred in methanol for 2-4

Table

Series No.	Aldehyde	Condensation product	Yield, %	Color	Melting point	Analysis (%) Nitrogen Calc.	Nitrogen Found	Sulfur Calc.	Sulfur Found
1	Butyraldehyde $CH_3CH_2CH_2CHO$		74	Light yellow	228-230	7.86	7.80	9.00	8.86
2	Heptanol $CH_3(CH_2)_5CHO$		83	"	158-160	6.36	6.34	7.27	7.34
3	Decanal $CH_3(CH_2)_8CHO$		50	"	110-113	5.35	5.20	6.12	6.10
4.	p-Dimethylamino-benzaldehyde 		65	Greenish Yellow	231-232	10.98	10.90	6.27	6.73
5.	Vanillin 		76	Orange	42-44	5.43	4.80	6.20	6.26
6.	Cotarnine 		74	Grayish	155-156	8.16	8.20	4.66	4.90
7.	α-Naphthaldehyde 		60	Light yellow	74-76	5.34	5.38	6.10	6.33
8.	Furfural 		77	Brown	300 decomp.	6.93	6.34	7.92	7.70
		Condensation with Promuzole							
9.	Salicylaldehyde 		73	Orange	246-248	11.69	11.40	17.82	17.87
10.	p-Dimethylamino-benzaldehyde 		80	Orange	225-227	14.50	14.60	16.58	16.57

hours in a flask fitted with a reflux condenser. As a rule, both ingredients entered solution to begin with, a precipitate later settling out as a result of the reaction. When no precipitate was thrown down, the solvent was evaporated to a small residue after completion of the reaction. Depending on the nature of the residue, it was appropriately treated until a product suitable for analysis was recovered. Some examples of individual condensations are given below.

Condensation of Diaminodiphenylsulfone With Butyraldehyde

5 g of diaminodiphenylsulfone, 40 ml of methanol, and 3.5 g of butyraldehyde were placed in a flask fitted with a stirrer and a reflux condenser. Stirring was done at the boiling point. A precipitate began to settle out an hour or two after the reaction set in. Stirring was continued for another 2 hours. After cooling, the precipitate was separated on a suction filter and then washed several times with methanol and ether. After desiccation, it weighed 5.2 g (74%). The resulting reaction product is a slightly yellowish powder, with a m.p. of 242-245°. It is decomposed by acids and alkalies and is insoluble in water and in most ordinary organic solvents. The reaction product is readily soluble in acetone, however, from which it can be precipitated with alcohol. The isolated product fuses at a much lower temperature and over a wide range.

Condensation of diaminodiphenylsulfone with heptanal, p-dimethylaminobenzaldehyde, cotarnine, α-naphthaldehyde, and furfural was effected in the same way.

Condensation of Diaminodiphenylsulfone with Vanillin

1.25 g of diaminodiphenylsulfone, 30 g. of methanol, and 1.5 g of vanillin were placed in a flask fitted with a stirrer and a reflux condenser. All the ingredients entered solution after stirring for some time at 70-80°. The reaction was continued under these conditions for 4 hours. No precipitate was thrown down, even after chilling. The solution was evaporated in vacuum to a thick mass, which solidified after standing for 5 days in a vacuum exsiccator. The mass was pulverized to a yellow powder. This yielded 2.1 g (70%).

The substance is soluble in alcohol and acetone, but insoluble in ether. The product had a m.p. of 42-44° after having been washed with ether.

Condensation with decanal was effected in the same way.

Condensation of 4-aminophenyl-2'-aminothiazolyl-5'-sulfone (Promizole) with Salicylaldehyde

10.2 g of promizole, 14 g of salicylaldehyde, and 200 ml of methanol were placed in a flask fitted with a stirrer and a reflux condenser. The mixture was heated to the boiling point with constant stirring. At first all the ingredients entered solution, but after 20 minutes had elapsed a precipitate began to settle out. The reaction was continued for another two hours. After cooling, the reaction product was filtered out on a suction filter and washed with alcohol and ether. This yielded 13.6 g (73% yield) of reddish-orange crystals; m.p. 246-248° (with decomposition).

Condensation with p-dimethylaminobenzaldehyde was effected in the same manner.

In both cases only the amino group of the benzene ring condensed with the aldehyde.

Data on the condensation products are given in the table (cf p. 1372).

SUMMARY

A number of condensation products of aldehydes with 4,4'-diaminodiphenylsulfone and 4-aminophenyl-2'-aminothiazolyl-5'-sulfone have been synthesized.

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[2] Biochem. J., 31, 724 (1937).

[3] Brit. Patent No. 491625, C. A., 1939, 1104.

[4] C.A., 1942, 2687.

[5] French patent No. 845532, C. A., 1941, 1184.

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[7] C. A., 1946, 571.

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SULFONATION WITH SALTS OF SULFURIC ACID.

SULFONATION OF 1-NAPHTHYLAMINE AND 1-NAPHTHOL

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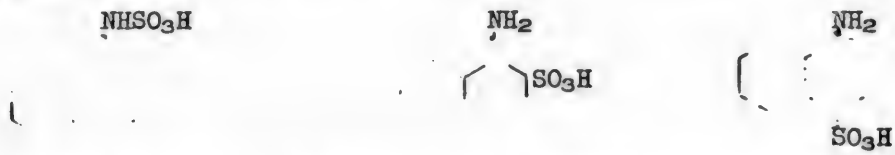
In one of our preceding reports [1], we noted that oxidation of a sulfite by manganese dioxide in the presence of 1-naphthylamine resulted in the formation of sulfo acids. The yield of sulfo acids was low, and their structure remained indefinite, but there were certain indications that one of them was anphthylsulfamic acid. Returning to this problem, we chose sodium mercuric sulfite $[Hg(SO_3)_2]Na_2 \cdot H_2O$, as the sulfonating agent, which exhibited its sulfonating ability during decomposition in an aqueous medium in the presence of 2-hydroxy-3-naphthoic acid and aniline [2]. Decomposition of the coordination compound in an aqueous emulsion of naphthylamine likewise resulted in the formation of sulfo acids of the latter, with a yield that was 18.5% of that computed from the equation:

$$[Hg(SO_3)_2]Na_2 + RH \longrightarrow Hg + NaHSO_3 + RSO_3Na,$$

three sulfo acids:



being formed thereby, in the approximate proportions of 9:29:62, respectively. (In analysis, the ratio of the phenylsulfamic acid to the anilinesulfo acids was 63:37, ortho anilinesulfonic acid being the isolated, and possibly the only, anilinesulfo acid.)

All the naphthol derivatives used by us in our research on their behavior with the sulfite and the oxidants belonged to the 2-naphthol series, and the sulfonation reaction was always carried out at position 1. The behavior of 1-naphthol also interested us.

Our experiments using sodium sulfite and manganese dioxide yielded naphthol oxidation products together with a very small quantity of 1-naphthol-4-sulfonic acid, possibly contaminated with isomers. Sulfonation of 1-naphthol by sodium mercuric sulfite, with no alkaline agents present, in a soda medium, or in the absence of water, resulted in a yield of sulfo acids in the optimum case that amounted to no more than 3.4% of the quantity computed from the foregoing equation. Nor did substituting sodium sulfite and mercuric oxide for the sodium mercury sulfite yield any better results. The principal sulfonation product was 1-naphthol-4-sulfonic acid, together with a small quantity of another sulfo acid, apparently, 1-naphthol-2-sulfonic acid.

EXPERIMENTAL

1. Sulfonation of 1-Naphthylamine

A mixture of 30 g of 1-naphthylamine, 21.3 g (0.05 mol) of sodium mercuric

sulfite, and 100 ml of water, was boiled for 2.5 hours with a reflux condenser and constant stirring; the sulfite was decomposed after 30-40 minutes had elapsed. The metallic mercury was removed from the reaction mass, and the latter was filtered with sodium hydroxide and then treated repeatedly with benzene to extract the naphthylamine. Part of the aqueous layer was strongly acidulated with hydrochloric acid, boiled to drive off the sulfur dioxide, and again acidulated, and the 1-naphthylamine formed during the hydrolysis of the N-sulfonic acid was extracted with benzene. After the benzene extract had been treated with hydrochloric acid, 0.131 g of the amine (0.00086 mol) (in terms of the aggregate volume) was found in the acid solution by titration with the nitrite; hence, the yield of the N-sulfonic acid was 1.72% of the sodium mercuric sulfite. In terms of the aggregate volume, 1.87 g of naphthylaminesulfo acids (0.0084 mol), or 16.8% of the sulfite, was found in the aqueous residue.

To ascertain the approximate proportions of the isomeric sulfo acids, the combined reaction solutions of several runs were evaporated to small volume after the naphthylamine had been eliminated, then boiled over a water bath, and set aside to stand overnight. The mixture of sulfo acids that settled was filtered out and dissolved in soda, the solution being then treated with benzene and evaporated to dryness.

The mixture of sodium sulfonates was heated with aqueous alcohol; the salt of the 1,4-isomer principally went into solution, the 1,2-isomer remaining in the residue. The ratio of the 1,4 to the 1,2 isomers (according to the nitrite analysis) was 68.5: 31.5.

The sodium salt of the 1,2 isomer consisted of yellowish lamellae after recrystallization from water.

0.2506 g substance: losses in drying (110°) 0.0068 g
0.2386 g of dry substance: 0.0687 g Na_2SO_4.
Found %: H_2O 2.71; Na 9.32.
$C_{10}H_8O_3NSNa \cdot 0.5H_2O$. Calculated %: H_2O 3.54.
$C_{10}H_8O_3NSNa$. Calculated %: Na 9.38.

The diazo compound – a greenish-yellow precipitate – yields a purple dye with an H acid in a soda medium and a reddish-orange dye with 2-naphthol.

1-Chloronaphthalene-2-sulfonic acid, -sulfochloride, and -sulfamide. 3 g of sodium aminosulfonate in a small quantity of water was acidulated with 6.5 ml of hydrochloric acid and diazotized with 0.9 g of the nitrite. The diazo compound was placed in a solution of 1.6 g of copper sesquichloride in 16 ml of hydrochloric acid heated to 80°, and heating was continued until foaming stopped. The liquid was diluted with water and alkalized; the copper filtrate was evaporated until an orange substance began to crystallize out. After chilling, the sodium chloronaphthalenesulfonate was filtered out and desiccated at 105°.

1.5 g of the sodium salt was triturated with 1.5 g of phosphorus pentachloride, and the mixture was set aside to stand for 20 hours with no moisture present, after which it was poured over ice. The sulfochloride that settled out was filtered out and recrystallized from benzene; m.p. 81°.

The sulfochloride was triturated with 25% ammonia, and the amide was filtered out and recrystallized from water and alcohol. A colorless, almost insoluble powder, that did not fuse up to 251°.

After crystallization from alcohol, the sodium salt of the 1,4 isomer consisted of rhombic platelets; they were analyzed after being dessicated at 100°.

0.5022 g substance: losses in drying (130°) 0.0181 g.
0.2924 g of dry substance: 0.0858 g Na_2SO_4.
Found %: H_2O 3.60; Na 9.50.
$C_{10}H_8C_3NSNa \cdot 0.5\ H_2O$. Calculated %: H_2O 3.54.
$C_{10}H_8O_3NSNa$. Calculated %: Na 9.38.

The diazo compound, a yellowish precipitate, forms a raspberry-red dye with an H-acid, and a yellow-orange dye with 2-naphthol.

1-Chloronaphthalene-4-sulfonic acid, -sulfochloride, and -sulfamide were synthesized like the 1,2 isomer.

The m.p. of the sulfochloride, crystallized from benzene, was 91.5°, and that of the amide, crystallized from water, was 184°.

2. Sulfonation of 1-Naphthol

a) The reaction was carried out like that with the 1-naphthylamine. After chilling, the mercury and the excess naphthol were filtered out, and the filtrate was acidulated with sulfuric acid and treated with ether. The aqueous solution was evaporated to remove the sulfuric acid, and then it was analyzed by combining it with diazobenzene or by nitrosation. 0.222 g of the naphthol (0.001543 mol) entered into the sulfonation reaction, i.e, the yield of the sulfo acids was 3.08% of the sulfite.

b) 10.7 g (0.025 mol) of sodium mercury sulfite was added to a mixture of 30 g of the naphthol, 1.35 g (0.013 mol) of soda, and 100 ml of water, heated to 90°, and the mixture was boiled for 2 hours, after which the same amounts of soda and sulfite were again added, and boiling was continued for another 6 hours. Part of the sulfite remained undecomposed. 0.245 g (0.0017 mol) of the naphthol was converted into the sulfo acid; the yield of sulfo acids was 3.4% of the sulfite.

The result was not changed by prolonging the period of boiling to 16 hours.

c) 30 g of the naphthol and 21.3 g of sodium mercuric sulfite were heated for 6 hours at 100-104°; part of the sulfite remained unchanged. 0.106 g (0.00074 mol) of the naphthol was converted into a sulfo acid; the sulfo acid yield was 1.48% of the sulfite.

d) 0.1 mol of freshly precipitated mercuric oxide was added to a mixture of 30 g of the naphthol, 40 ml of sodium bisulfite (0.2 mol), 8.5 ml (0.05 mol) of 20% sodium hydroxide, and 100 ml of water, and the mixture was boiled. The resulting gray precipitate gradually gave off metallic mercury, but it did not decompose completely even after 6 hours of boiling. 0.293 g of the naphthol was converted into the sulfo acid.

In the same experiment, but without any alkali used, 0.65 g of the naphthol was converted into the sulfo acid after 2.5 hours of boiling.

The sulfo acids were recovered from solutions collected from several experiments by evaporating them to dryness and extracting the residues with alcohol. The brown precipitate obtained by evaporating the alcoholic extract was dissolved in water, and the solution was decolorized with charcoal and saturated with potassium chloride (15 g of potassium chloride was used for 50 ml of the solution, containing 1 g of the sulfo acids). The 1,2-isomer ought to precipitate out, with the 1,4 isomer remaining in solution [3]. The precipitated deposit was very slight; its solution (first washed with ether) formed a yellowish-red precipitate when combined with diazobenzene and a brownish-red precipitate with diazo-p-nitrobenzene; both precipitates dissolved when heated. Yellowish-red and purple solutions were produced by reacting these diazo compounds with the filtrate.

When reacted with nitrous acid, the filtrate yielded yellow needles of 2-nitroso-1-naphthol-4-sulfonic acid, which were identified by the formation of the green iron salt, its conversion into 2,4-dinitro-1-naphthol (m.p. 137°) when heated with nitric acid, and the formation, when reduced with zinc powder and acetic acid, of a colorless solution, that quickly turned blue, with acid changing its color to red and alkali changing it to green. When reduced with stannous chloride, the nitroso compound was transformed into 2-amino-1-naphthol-4-sulfonic acid, the diazo compound of which (synthesized in the presence of copper sulfate) turned fuchsine red with resorcinol, the product of nitric-acid oxidation being 1,2-naphthoquinone--4-sulfonic acid. All this indicates that the naphthosulfo acid in the filtrate was 1-naphthol-4-sulfonic acid.

In our experiments on sulfonation with sulfite and manganese, 0.15 mol of manganese was added in the course of 15-30 minutes to a mixture of 0.1 mol of the naphthol, 0.3 mol of sodium sulfite (or bisulfite, neutralized 25 and 50%), and 150 ml of water, and the mixture was boiled for 1 hour. The filtrate obtained after the residual naphthol is eliminated was orange-yellow and contained a considerable amount of the sulfite. When the acidulated solution was evaporated, only mineral salts were thrown down. When the end filtrate was evaporated to dryness, there remained a small quantity of a brownish, highly soluble residue, which we were unable to purify. When reacted with nitrous acid, it yielded 2-nitroso-1-naphthol-4-sulfonic acid and, hence, was a contaminated 1,4-sulfo acid.

SUMMARY

1. When 1-naphthylamine is reacted with sodium mercury sulfite, 1-naphthylsulfamic acid, 1,2-naphthylaminesulfonic acid, and 1,4-naphthylaminesulfonic acid are synthesized in the proportions of 9: 29: 62, respectively.

2. Sulfonation of 1-naphthol with sulfite and manganese dioxide or with sodium mercury sulfite is slight; the principal product of sulfonation is 1,4-naphtholsulfonic acid.

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SYNTHESIS OF QUINUCLIDINE

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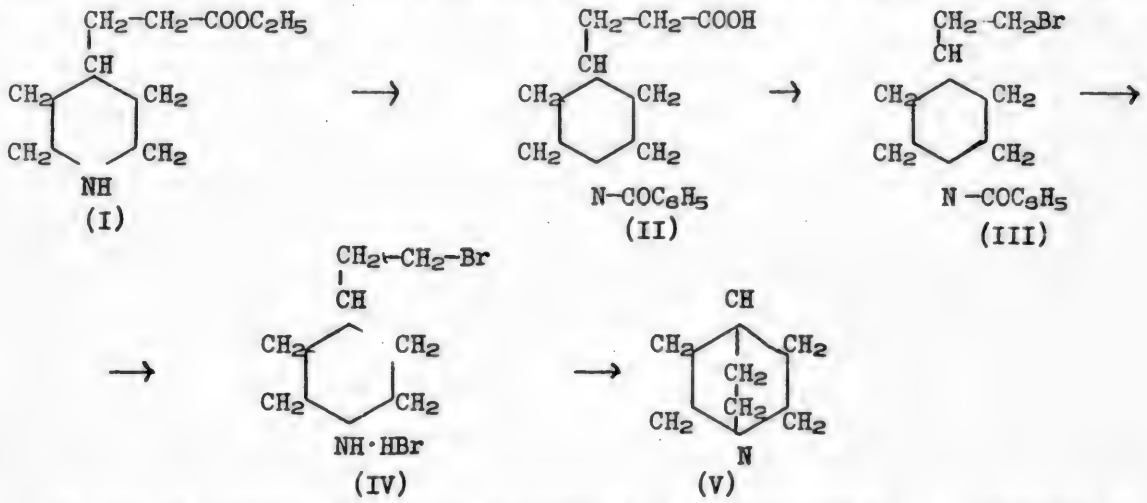
Quinuclidine is a heterocyclic, bicyclic system that is a constituent of quinine alkaloids.

Quinuclidine was first synthesized by Loffler and Stietzel [1] in 1909.

The first stage in this synthesis – the formation of 4-(β-oxyethyl)-pyridine [2] – results in a yield of 1.2 - 1.5% , which makes the yield of quinuclidine about 0.4%, based on the γ-picoline.

Subsequently, Prelog and his co-workers published a synthesis of quinuclidine, based in tetrahydropyranacetic acid, elaborating several methods for preparation of the latter [3]. The method proposed by them involved many states, however (11-12), and thus possessed no real advantages. The method described by Clemo and Metcalfe [4] is simpler and more convenient. In this latter method, the yield of quinuclidine was approximately 1.7%, based on the α-picoline.

We have developed a new variant of the synthesis of quinuclidine, which makes it possible to prepare it with a higher yield, indicated by the following diagram:



The initial product was ethyl β-[piperidyl-(4)]-propionate [1], prepared in the usual manner from γ-picoline [5]. The ester is saponified with potassium hydroxide, and the resulting salt of β-[piperidyl-(4)]-propionic acid is converted without prior separation into β-[N-benzoylpiperidyl-(4)]propionic acid (II). The silver salt of the latter is treated with bromine in carbon tetrachloride [6], resulting in the replacement of the carboxyl group by bromine and giving rise to β-[N-benzoylpiperidyl-(4)]-ethyl bromide (III). The unrefined bromide, recovered with a yield of 64.6%, is a thick yellow oil, which can be easily purified by means of a 2:1 mixture of ether and pentane, which transforms it into a white crystalline powder. The yield of the refined product was 42%.

When β-[N-benzoylpiperidyl-(4)]-ethyl bromide is boiled with 48% hydrobromic acid, it is converted into the hydrobromide of β-[piperidyl-(4)]-ethyl bromide (IV), with a yield of 60.7%. The use of less concentrated hydrobromic acid, say, 24%, yields poorer results, apparently because of the partial hydrolysis of the bromide and the formation of the corresponding hydroxy derivative.

Treatment of the hydrobromide of β-[piperidyl-(4)]-ethyl bromide with a dilute solution of sodium hydroxide yields 60% of quinuclidine (V).

The yield of quinuclidine was 3.6%, in terms of the -picoline. When unrefined β-[N-benzoylpiperidyl-(4)]-ethyl bromide is used, the quinuclidine yield rises to 4.28%.

EXPERIMENTAL

β-[N-benzoylpiperidyl-(4)]-propionic acid (II). 26 g of the hydrochloride of ethyl β-piperidyl-(4)]propionate was mixed with 175 g of 15% potassium hydroxide solution. The mixture was heated to a gentle boil for 2 hours. The resulting solution was cooled to 45°, and 19.6 g of benzoyl chloride was added during 15 minutes, with constant stirring, after which stirring was continued for another 30 minutes at the same temperature. Then the reaction mixture was chilled, the excess benzoyl chloride extracted with ether, and the mechanical impurities filtered out of the solution, which was acidulated with hydrochloric acid until its reaction with Congo red was acid. The oil that separated out soon crystallized. The precipitate was pulverized in a mortar, filtered, washed with water until the wash water no longer exhibited an acid reaction with Congo red, and desiccated in vacuum while the temperature was gradually raised to 100°. A white crystalline powder with a m.p. of 146-148°. The yield was 28.7 g, or 93.6% of the theoretical. The substance is readily soluble in chloroform and hot alcohol, but poorly soluble in ether. It crystallizes from alcohol as white needles that fuse at 148-150°.

3.623 mg substance: 9.186 mg CO_2; 2.267 mg H_2O.
6.036 mg substance: 0.305 ml N_2 (22°, 736.8 mm).
Found %: C 69.15; H 7.00; N 5.66.
$C_{15}H_{19}O_3N$. Calculated %: C 68.90; H 7.27; N 5.36.

The silver salt of the acid is prepared in a quantitative yield when the following conditions are maintained: a hot solution of 28.7 g of the acid in 111.9 ml of 1 N NaOH and a hot solution of silver nitrate in 38 ml of water are poured simultaneously into 20 ml of hot water, with constant stirring. After chilling, the white precipitate of the silver salt is filtered out, washed with water, and desiccated in the dark, first in air at room temperature, and then in vacuum at 50-60°.

β-[N-benzoylpiperidyl-(4)]-ethyl bromide (III). 34 g of the finely powdered silver salt of β-N-benzoylpiperidyl-(4)]-propionic acid was mixed with 300 ml of anhydrous carbon tetrachloride, after which part of the carbon tetrachloride (100 ml) was driven off to dehydrate the salt more completely. 14.7 g of anhydrous bromine was added over the course of 30 minutes to the remaining well-stirred mixture at 0°; then the mixture was heated for 30 minutes over a boiling water bath. After the reaction mass had been chilled, the silver bromide was filtered out and well washed with carbon tetrachloride. The filtrate was agitated with 16 ml of a 15% soda solution and desiccated with potash. Driving off the solvent yielded 17.7 g of the crude bromide as a light-brown thick oil, which partially crystallizes upon standing for a long time.

The crude product was dissolved in 40 ml of absolute ether and 20 ml of pentane was added to the solution. After standing for some time the solution was decanted from the thick brown oil (A) that separated out. Driving off the solvent and eliminating its last traces in a vacuum at 70° yielded a light yellow oil, which crystallized readily when rubbed with a glass rod. The substance was trans-

ferred to a filter and washed with a small quantity of absolute ether, chilled to 12°. When the wash ether was evaporated, there remained a semisolid mass (B).

Retreatment of the oily residues A and B by the method outlined above yielded some more of the bromide. The aggregate yield was 11.5 g, or 42% of the theoretical. The substance was a white crystalline powder with a m.p. of 62-65°; it is readily soluble in alcohol, acetone, chloroform, and ether at room temperature, and is poorly soluble in absolute ether at 10°. The substance fused at 63.5-65.5° after recrystallization from three times its weight of absolute ether.

3.820 mg substance: 2.361 mg AgBr.
Found %: Br 26.3.
$C_{14}H_{18}ONBr$. Calculated%: Br 27.0.

Hydrobromide of β-[piperidyl-(4)]-ethyl bromide (IV). 0.5 g of β-[N-benzoyl-piperidyl-(4)]-ethyl bromide, with a m.p. of 62-65°, was dissolved in 5 ml of 48% hydrobromic acid, and the solution was heated to a gentle boil for 1½ hours. After chilling, the solution was extracted with ether to remove the benzoic acid and then evaporated in vacuum over a water bath. Absolute alcohol was repeatedly added to the residue and then driven off in vacuum, after which the residue was dissolved in 2 ml of absolute alcohol, and the solution diluted with 15 ml of absolute ether. The resulting precipitate was filtered out, washed with ether, and desiccated in a vacuum exsiccator over sulfuric acid. This yielded 0.28 g of a crystalline powder with a m.p. of 175-177°. The yield was 60.7%. The substance was recovered in the form of minute white prisms (under the microscope), fusing at 180-181°, by recrystallization from an equal quantity of absolute alcohol. The crystals are readily soluble in water and in alcohol, but are poorly soluble in acetone and dichloroethane.

4.330 mg substance: 4.879 mg CO_2; 2.222 mg H_2O.
0.1076 g substance: 0.1464 g AgBr.
Found %: C 30.73; H 5.74; Br 57.9.
$C_7H_{14}NBr \cdot HBr$. Calculated %: C 30.76; H 5.49; Br 58.6.

Quinuclidine (V). 7.8 ml of 1 N NaOH (20% excess) was added to 0.9 g of the hydrobromide of β-[piperidyl-(4)]-ethyl bromide dissolved in 90 ml of water, after which the mixture was heated to 70° for 1½ hours with a reflux condenser. The flask was then connected to a straight-run condenser, and the aqueous quinuclidine solution was driven off until the distillate no longer exhibited an alkaline reaction to litmus. About 75 ml were driven off. 10 ml of a 5% alcoholic solution of picric acid was added to the distillate, which contained the quinuclidine. Light-yellow needles separated out. The precipitate was filtered out, washed with water, and desiccated at 100°. This yielded 0.673 g of quinuclidine, with a m.p. of 275-276°.* The yield was 60% of the theoretical.

Quinuclidine hydrochloride. The picrate, synthesized above, was mixed with approximately ten times its own weight of 17% hydrochloric acid, and the mixture was heated for 10 minutes over a water bath. Then the picric acid was extracted with nitrobenzene, and the latter was leached out with ether; the resulting colorless solution of quinuclidine hydrochloride was evaporated to dryness over a water bath. The residue was recrystallized from absolute alcohol. Minute white prisms, fusing at 315° (in a sealed capillary). The substance is readily soluble in water, 96% alcohol, and chloroform; somewhat less readily in absolute alcohol, and poorly in acetone.

0.0742 g substance: required 4.95 ml 0.1 N $AgNO_3$.
Found %: Cl 23.7.
$C_7H_{13}N \cdot HCl$. Calculated %: Cl 24.0.

*Meisenheimer gives the m. p. as 275-276°. [2].

SUMMARY

The synthesis of quinuclidine, starting with β-[piperidyl-(4)]-propionic acid and passing through the corresponding N-benzoyl derivative and β-[N-benzoyl-piperidyl-(4)]-ethyl bromide, has been described.

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RESEARCH ON THE ALKALOIDS OF HELIOTROPIUM SUPINUM

I. THE NEW ALKALOID SUPININE AND ITS STRUCTURE

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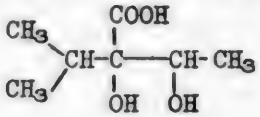
From a comparatively large quantity of a mixture of bases, obtained by the customary extraction from the Central Asiatic plant Heliotropium supinum, belonging to the Borraginaceae family, we have been able up to now to isolate one crystalline alkaloid in the pure state, the percentage of which in the plant does not exceed 0.05%. This alkaloid crystallizes from acetone as beautiful snow-white needles, which fuse at 146-147.5°; it is a strongly laevo-rotatory ($[\alpha] = -23.81°$) base and its composition is $C_{15}H_{25}O_4N$. To judge by its reduction of permanganate in a solution of dilute sulfuric acid, it is clearly unsaturated. The properties and constants of the alkaloid recovered from Heliotropium supinum differ from those of all substances described hitherto, and we propose to call it "supinine."

As with all the alkaloids of the Borraginaceae family examined by us up to the present time, supinine is an ester. Its alkaline hydrolysis results in the formation of the already known racemic trachelantinic acid, previously isolated by us by hydrolyzing the alkaloids trachelantamine [1], lindelofine, and lindelofamine [2], and the new, optically active unsaturated amino alcohol $C_8H_{13}ON$ called supinidine in accordance with the nomenclature we have adopted for the products of hydrolysis of the alkaloids of the Borraginaceae family. As one of the present authors has demonstrated, trachelantinic acid has the structure of 2-methyl-3,4-dihydroxypentane-3-carboxylic acid (I) [3]. Hence, all we need to determine of supinine is the structure of the amino alcohol supinidine. This was accomplished by means of three catalytic reductions. First, the supinine was exhaustively reduced with platinum prepared by Adams' method. 2 mols of hydrogen were absorbed, and the following reaction products were isolated: a base with the composition $C_8H_{15}N$, identical with 1-heliotridane [4], and trachelantinic acid, which exhibited extremely slight, but nonetheless noticeable, optical activity* ($[\alpha]_D = +1.30°$). This reduction proved that the mother substance of supinidine is 1-heliotridane, the structure of which is 1-methylpyrrolizidine (II) [5], as we know.

To ascertain the location of the hydroxyl group, the supinidine was reduced with Rainey nickel. 1 mol of hydrogen was absorbed. Only the double bond was reduced, and a saturated amino alcohol with the composition $C_8H_{15}ON$ was recovered; this latter was identified by direct comparison as isoretronecanol, synthesized from platinecine by the Adams method [6]. Since isoretronecanol has the structure of 1-hydroxymethylenepyrrolizidine (III), as Adams has demonstrated, this catalytic reduction proved the location of supinidine's hydroxyl group. This left only one problem to be cleared up, namely, the position of the double bond. This problem can be solved, however, by analyzing the results of these two catalytic reductions. In fact, as we have seen, when supinine is reduced with platinum, not only is the double bond reduced, but the hydroxyl group as well, whereas the hydroxyl group of the double-bond-reduced supinidine, i.e., isoretronecanol, is not reduced under these conditions. We must therefore conclude that the double bond is responsible for the ready reduction of supinidine's hydroxyl group. And this can

*Evidently, the racemic trachelantinic acid previously synthesized by the alkaline hydrolysis of supinine and other alkaloids was racemized by the action of the hot alkaline solution.

take place only if the bond is one carbon atom away from the hydroxyl group, i.e., if the alcohol is an allyl one. Hence, the double bond must connect either the 1 and 2 or the 1 and 7 carbon atoms of the pyrrolizidine ring. The possibility of the latter position is excluded, however, by supinidine's optical activity. It is actually easy to see that the asymmetrical centers of the bicyclic system of 1-methylpyrrolizidine are located only at positions 1 and 7. If the double bond were also located between these two carbon atoms, both asymmetrical centers would be disrupted, and supinidine could not exhibit any optical activity. It must therefore be concluded that the double bond lies between carbon atoms 1 and 2. This conclusion was confirmed experimentally by reducing supinine with platinum, as before, but breaking off the reduction process as soon as 1 mol of hydrogen had been absorbed. This resulted in the reduction of the hydroxyl group principally, and, in addition to the trachelantinic acid, we obtained an unsaturated base that yielded a picrate with a m.p. of 198-199°. This is the same as the melting point of the picrate of isoheliotridene, which Adams synthesized by eliminating two hydroxyl groups from retronecine. As this researcher has proved, isoheliotridene has the structure of 1-methylpyrrolozidine, with the double bond between carbon atoms 1 and 2 [7]. Obviously, the double bond must also lie between these atoms in supinidine as well. Hence, supinidine must possess structure (IV), if we bear in mind the position of the hydroxyl group proved above. The alkaloid must have structure (V) as an ester of supinidine and trachelantine acid.



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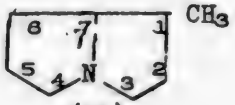

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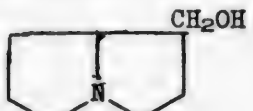

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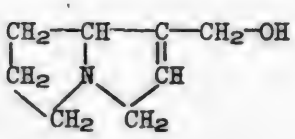
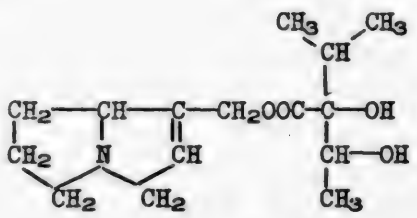


(IV)



(V)

In conclusion, we wish to take this oppprtunity to thank P.S.Masaagetov for the plant material placed at our disposition for the present research.

EXPERIMENTAL

Isolation and purification of supinine. 5 kg of the ground-up air-dried, above-ground parts of the plant was treated with 10% ammonia until a strong odor was produced, and then extracted exhaustively with dichloroethane. The alkaloids were extracted from the dichloroethane solution by a 10% solution of sulfuric acid. The acid solution was filtered, treated with strong ammonia until its odor was strong, and extracted with ether. The ether solution was desiccated over sodium sulfate and filtered, after which the ether was driven off. There remained a yellow oil (about 17 g), part of which crystallized upon standing. This mixture was treated with a small quantity of acetone. This caused the oil to enter solution, leaving behind large, nearly white needles. These crystals were filtered out on a suction filter, washed with a small quantity of acetone, and dissolved in 0.5 N hydrochloric acid for further refining. The small amount of undissolved impurities was filtered out of the solution, which was then alkalized with 0.5 N sodium hydroxide, the same quantity of the latter being used as of the hydrochloric acid previously. This caused colorless needles to settle out; they were separated on a suction filter, washed with water and then with acetone, and recrystallized from acetone (1:40). This yielded about 2 g of large snow-white needles, which fused at 146-147.5°.

0.4954 g substance: in 10 ml of ethanol: $\underline{l} = 1$; $\alpha_D = -1{\cdot}18°$; $[\alpha]_D = -23.81°$.

3.233 mg substance: 7.539 mg CO_2; 2.521 mg H_2O.
2.980 mg substance: 6.956 mg CO_2; 2.310 mg H_2O.
7.675 mg substance: 0.343 ml N_2 (15.5°, 736 mm).
8.675 mg substance: 0.392 ml N_2 (15°, 736 mm).
Found %: C 63.60, 63.66; H 8.72, 8.67; N 5.12, 5.19.
$C_{15}H_{25}O_4N$. Calculated %: C 63.56; H 8.89; N 4.95.

Supinine is rather poorly soluble in water and in cold acetone; it dissolves readily in alcohol. Up to the present, we have been unable to isolate anything from the mixture of acetone-soluble alkaloids that accompanies the supinine.

Saponification of supinine. 2 g of the alkaloid was dissolved in 40 ml of ethanol. 40 ml of a 20% solution of sodium hydroxide was added to the solution, and the whole was heated for 1.5 hours with a reflux condenser over a water bath. The ethanol was driven off from the solution in vacuum (30 mm), and the remaining aqueous solution was extracted with ether. The ether extract was dried with potash, and the ether was driven off. The remaining light-yellow oil (0.9 g) was distilled in vacuum. Almost all of it distilled over at 158-159° (10 mm). The substance did not crystallize upon standing.

0.6560 g substance; in 10 ml of ethanol: $\underline{l} = 1$; $\alpha_D = -0.62°$; $[\alpha]_D = -9.45°$.

3.211 mg substance: 8.102 mg CO_2; 2.759 mg H_2O.
5.089 mg substance: 12.810 mg CO_2; 4.349 mg H_2O.
8.608 mg substance: 0.760 ml N_2 (25.5°, 739 mm).
5.200 mg substance: 0.456 ml N_2 (26.5°, 738 mm).
Found %: C 68.81, 68.63; H 9.61, 9.56; N 9.81, 9.70.
$C_8H_{13}ON$. Calculated %: C 69.02; H 9.42; N 10.07.

The amino alcohol is readily soluble in water and in the ordinary organic solvents; it instantaneously reduces a solution of permanganate in dilute sulfuric acid. The alkaline solution left after the amino alcohol had been extracted was acidulated with 20% hydrochloric acid until it gave an acid reaction with Congo red, after which it was repeatedly extracted with ether. The ether solution was desiccated with sodium sulfate, and the ether was driven off. The residue soon crystallized completely. The crystalline mass was recrystallized from a mixture of chloroform and petroleum ether. This yielded 0.8 g of a crystalline deposit, all of whose properties were the same as those of racemic trachelantinic acid.

Supinine picrate. This salt is precipitated out when alcoholic solutions of the base and of picric acid are mixed together. After recrystallization from alcohol, it consists of yellow needles, rather poorly soluble in water and alcohol, which fuse at 142-143°.

2.758 mg substance: 0.370 ml N_2 (20.5°, 745 mm).
2.904 mg substance: 0.391 ml N_2 (20.5°, 745 mm).
Found %: N 15.29, 15.35.
$C_8H_{13}ON \cdot C_6H_3O_7N_3$. Calculated %: N 15.22.

Total reduction of supinine with platinum by the Adams method. 3 g of the alkaloid was treated with 1 N hydrochloric acid until its reaction with Congo red was acid. Platinum (from 0.5 g of H_2PtCl_6), was added to the solution, and the whole was shaken up in a hydrogen atmosphere at slightly over atmospheric pressure. About 500 ml of hydrogen (2 mols) were absorbed in two hours, and absorption came to an end. The platinum was filtered out of the acid solution, which was then repeatedly extracted with ether. Driving off the ether left behind a crystallizing oil, which yielded a precipitate of minute acicular crystals after being recrystal-

lized from a mixture of chloroform and petroleum ether; these crystals fused at the same temperature as did racemic trachelantinic acid (93-94°), and exhibited no depression of the melting point in a mixed test sample with the latter. The resulting acid exhibited a very slight, but nonetheless observable specific rotary power: 0.5090 g of substance: in 11 ml of water; $\underline{l} = 1$; $\alpha_D = +0.06$; $[\alpha]_D = +1.30°$. The acid solution from which the trachelantinic acid had been extracted was treated with an excess of 40% sodium hydroxide and then extracted with a small quantity of ether. The ether solution was desiccated with potash, and the ether was driven off with a dephlegmator. The residual oil was distilled at normal pressure. This yielded 1.1 g of a base, which was identified as l-heliotridane by direct comparison. Not only the base itself, but the salts: the picrate and the picrolonate, were compared.

Reduction of supinidine with Rainey nickel. 0.8 g of supinidine, 25 ml of ethanol, and 1 g of the catalyst were shaken together in a hydrogen atmosphere at slightly over normal pressure until no more hydrogen was absorbed. The catalyst was filtered out of the alcohol solution, which was acidulated with 1 N hydrochloric acid until its reaction with Congo was acid and then reduced in vacuum to small volume. The concentrated solution was alkalized with 20% sodium hydroxide and then extracted with ether. The ether solution was desiccated with potash, and the ether was driven off. The residue was distilled in vacuum. This yielded 0.5 g of a crystallizing oil, which was identified as isoretronecanol by direct comparison with the iscretronecanol prepared for the purpose from platinecine by the Adams method. The picrates of these amino alcohols were also compared; they fused at the same temperature (193-194°): and exhibited no depression of the melting point in a mixed test sample.

Partial reduction of supinine with platinum by the Adams method. 2 g of the alkaloid was treated with 1 N hydrochloric acid until its reaction with Congo was acid. The catalyst (made from 0.5 g of H_2PtCl_6), was added to the solution, and the whole was shaken in an atmosphere of hydrogen at slightly over normal pressure. When 155 ml (1 mol) of hydrogen had been absorbed, agitation was stopped, and the catalyst was filtered out of the solution. The trachelantinic acid was extracted from the latter with ether; the acid likewise possessed a very slight amount of optical activity. The acid solution from which the trachelantinic acid had been extracted was concentrated to small volume in vacuum, treated with a large excess of 40% sodium hydroxide, and extracted with a small quantity of ether. The ether was driven off with a dephlegmator, and the dark-yellow oil that was left was distilled with steam. The base was salted out of the distillate with 40% sodium hydroxide and then extracted with ether. The ether solution was desiccated with potash, and the ether was driven off with a dephlegmator. What was left was a nearly colorless oil (0.6 g). A small quantity of this oil was used to prepare the picrate, the broad melting point of which indicated that this product was not a homogeneous substance. It was conjectured that it was a mixture of the unsaturated base and the unsaturated heliotridane, which could be formed by the complete reduction of the amino alcohol. This was explored by dividing the mixture into 3 fractions according to their basicity. This was done by titrating the product against Congo with 0.5 N hydrochloric acid and, as soon as the solution had turned acid, adding to it a quantity of 0.5 N sodium hydroxide equal to one third of the hydrochloric acid required for titration. Then the solution was carefully extracted with ether, and the same quantity of 0.5 N sodium hydroxide was again added. This operation was performed three times. This yielded 3 ether solutions of the bases, of different basicity. All these solutions were desiccated with potash, and the ether driven off with dephlegmators. After the ether had been driven off, what was left of the first fraction was a nearly colorless, mobile oil, an alcoholic solution of which yielded a picrate that fused with decomposition at 198-199° after being recrystallized from alcohol. This is the melting point of the picrate of isoheliotridene, synthesized by Adams from retronecine. The picrates obtained from the second and

third fractions had higher, but broader melting points (205-212°), which indicated that they were mixtures of picrates of isoheliotridene, and, most likely, heliotridane.

SUMMARY

1. A new alkaloid, $C_{15}H_{25}O_4N$, called "supinine", has been isolated from Heliotropium supinum.

2. It has been proved that supinine is an ester of the already known trachelantinic acid and an unsaturated amino alcohol (supinidine) with the composition of $C_8H_{13}ON$.

3. Exhaustive reduction of supinine with platinum yielded optically active trachelantinic acid (I) and l-heliotridane (II).

4. Reduction of supinidine with nickel (by the Rainey method) yielded isoretronecanol (III), which fixed the position of the hydroxyl group.

5. Partial reduction of supinine with platinum yielded isoheliotridene, which fixed the position of the double bond. Hence, supinidine must possess structure (IV), and the alkaloid itself must have structure (V).

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ACONITE ALKALOIDS

IV. DELARTINE

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The present paper is a continuation of the research instituted in our laboratory on the alkaloids of various species of delphinium [1,2] that grow on the territory of the USSR. Previously, we had been able to show that the condelphine isolated from Delphinium confusum [2] was an acetyl derivative of isotalatisidine, synthesized by one of the present authors [3] from Aconitum talassicum.

Somewhat later the British researcher Goodson [4] confirmed this bond between the alkaloid methyl lycaconitine, isolated from Delphinium elatum, and lycaconitine, isolated from Aconitum lycoctonum [5], as it was found that both alkaloids yield the same amino alcohol – lycoctonine – when cleaved hydrolytically. These facts justify our combining our research on the delphinium alkaloids with the researches on the aconite alkaloids into a single group under the single heading "aconite alkaloids".

The present paper sets forth the results of our investigation of the alkaloids isolated from Delphinium sp. This species, supplied to us for research purposes by the director of the Central Asian Expedition, P.S. Massagetov, was collected near the Kyz-art Pass in the Central Tian Shan. Its exact species name has not been established as yet.

All the above-ground parts of the plant underwent extraction. The alkaloids recovered were separated according to their solubilities in ether and in chloroform.

The total alkaloids recovered from the chloroform fraction were 0.1% of the dry weight of the plant, as a thick, hyaline mass. When this latter was triturated with acetone, a crystalline, slightly colored powder was obtained, which fused at 190-196° after recrystallization from alcohol, formed a crystalline tartrate with a m.p. of 157-161°, and resembled the alkaloid delphamine [1] isolated by us from Delphinium sp in all of its properties. A mixed test sample did not exhibit any depression of the melting point, which confirmed the identity of the two bases.

Perusing the literature devoted to a study of the newly isolated alkaloids from various species of Delphinium, our attention was attracted by a paper of Goodson's [6], published in 1945, in which he reports the isolation of five bases from Delphinium ajacis, one of which was named "Alkaloid C."

In comparing the described properties of this last base with those of the delphamine just mentioned, one cannot but notice the great resemblance between them. For further identification, we synthesized the chloroaurite of delphamine and determined the specific rotatory power of the alkaloid in a solution of 0.5 N

hydrochloric acid.

The data listed in Table 1 justify our assuming that the two alkaloids are identical, but this identity can be definitely proven only by a direct comparison of delphamine with "Alkaloid C'.

TABLE 1

Constants	Delphamine	"Alkaloid C"
M.p. of the base.....	196-200.5° (with decomp.)	206° (with foaming at 200°)
m.p. of the chloroaurite...	171-172°	171°
$[\alpha]_D$ in alcohol	+54°	+ 57°
$[\alpha]_D$ in 0.5 N HCl.....	+34°	+36.4°
Functional groups.....	$(OH)_4(OCH_3)_3$ (NC_2H_5)	$(OH)_4(OCH_3)_3$ (NC_2H_5)
C, %.....	64.16, 64.03	63.8
H,%.....	8.88 8.81	8.6
N, %.....	3.04 3.05	3.5
Empirical formula.....	$C_{25}H_{41}O_7N$	$C_{24}H_{37}O_7N$

It is worthy of note that notwithstanding the fact that data of the elementary analyses are extremely close, the two bases are assigned different empirical formulas, which differ by one CH_4 group. If we bear in mind the high molecular weight of aconite alkaloids, this difference between the two empirical formulas should occasion no great surprise. But when we analyze these minimum formulas, we arrive at different conclusions regarding the nature of the ring system underlying these alkaloids. Thus, if we compare the partially expanded formulas of the two alkaloids, replacing all the functional groups by hydrogen, and the nitrogen by "CH" [7], we obtain the following expressions (Table 2).

TABLE 2

Base	Partially expanded formula	Supposed heterocyclic ring	Hypothetical hydrocarbon
Delphinium.....	$C_{20}H_{23}(OH)_4(OCH_3)_3(NC_2H_5)$	$C_{20}H_{31}N$	$C_{21}H_{32}$
"Alkaloid C"	$C_{19}H_{19}(OH)_4(OCH_3)_3(NC_2H_5)$	$C_{19}H_{27}N$	$C_{20}H_{28}$

Hence, provided no double bond is present (nothing is said in this respect concerning "Alkaloid C"), delphamine must be a derivative of a hypothetical hydrocarbon $C_{21}H_{32}$, consisting of a six hydrogenated rings, whereas "Alkaloid C" is the corresponding derivative of the hydrocarbon $C_{20}H_{28}$, consisting of seven hydrogenated rings. The available data on aconite alkaloids, however, indicate that the latter assumption is hardly likely, since the composition of nearly all the known alkaloids of this series is expressed by the formulas $C_{19}H_{29}N$ or $C_{20}H_{31}N$ [1,8]. Thus, the problem of the correct empirical formula of delphamine and "Alkaloid C" must be set aside as unsettled for the present.

We were unable to isolate any other individual substances, besides delphamine, from the chloroform fraction of alkaloids of this species of Delphinium.

The total alkaloids recovered from the ether fraction constituted 0.4% of the the dry weight of the plant, as a thick, transparent, hyaline mass. All our efforts to isolate crystalline bases from this fraction proved fruitless. After great labor, we succeeded merely in isolating a crystalline perchlorate, which was recovered as a colorless crystalline substance with a m.p. of 188-190° after repeated refining and recrystallization. According to its elementary analysis, the

perchlorate's composition is $C_{36}H_{53}O_{11}N_2 \cdot HClO_4$. The free base isolated from the perchlorate is a hyaline mass, which can be ground into an amorphous, light powder that does not have a sharp melting point. We named the alkaloid delartine (from the name of the place where this species grows).

We were able to isolate the saponification products of delartine – a crystalline amino alcohol and an acid, which we called delartinic acid – by hydrolyzing the alkaloid with an alcoholic alkali. Up to the present time, we have learned that delartinic acid is a complex acid, containing nitrogen, which is extremely hard to purify. By saponifying it further with hydrochloric acid we have succeeded in isolating two crystalline substances, one of which was identified as anthranilic acid. The nature of the other product of acid hydrolysis is as yet unknown.

The principal product of hydrolysis – the amino alcohol – crystallizes with one molecule of water and has a m.p. of 110-115°. After being desiccated in vacuum it turns into an amorphous, hyaline substance, with a m.p. of 137-142°. The amino alcohol fuses at the same temperature after being recrystallized from anhydrous benzene. The base forms salts that crystallize well: the hydrobromide, hydrochloride, perchlorate, and hydriodide. The hydriodide is prepared by heating the base in a sealed tube with methyl iodide. According to the elementary analyses of both the base itself and its salts, the formula of the base is $C_{28}H_{43}O_7N$. Catalytic hydrogenation (by the Adams method) yielded the base unchanged, which indicated the saturated nature of the substance. Determination of the amino alcohol's functional groups indicated that it contained three free hydroxyl groups and four methoxy groups, which established the function of all the seven oxygen atoms. To ascertain the nature of the N-alkyl group, we subjected the delartine to oxidation with potassium permanganate, as we had done with delphamine [1] and condelphine [2]. Here again, we were able to isolate acetaldehyde, which was proved by the recovery of its condensation product with dimedon. Thus the nitrogen is attached to the ethyl group in delartine as well.

When we compared the properties of the amino alcohol derived from delartine with those of the amino alcohols of other aconite alkaloids, we were struck by the great resemblance between it and lycoctonine.

Lycoctonine was first isolated by Hubschmann in 1865 from Aconitum lycoctonum. The subsequent researches of Dragendorf [5] established that lycoctonine is a product of the alkaline hydrolysis of lycaconitine. Many research workers were engaged in its study, Schulze [9] having made notable contributions. The latter defined the composition of lycoctonine, assigning it the formula $C_{25}H_{39}O_7N$, and established that it contained four methoxyl and methylimide groups and two hydroxyl groups. Schulze considered lycoctonine to be a strong base, which formed a characteristic iodomethylate. Lycoctonine was later isolated from Delphinium elatum by Goodson [4] as a product of the alkaline hydrolysis of methyllycaconitine: methylsuccinylanthranoyllycoctonine. This same researcher [8] established that lycoctonine has three hydroxyl groups and that an ethyl group is attached to the nitrogen, as is the case with delphamine and condelphine. Goodson also isolated lycoctonine [10] by hydrolyzing ajacine, an alkaloid obtained from Delphinium ajacis, which is acetylanthranoyllycoctonine. All the described properties of lycoctonine resemble the properties of the amino alcohol of delartine so closely that we may take them to be identical (Table 3).

As Table 3 indicates, here again (as in the case of delphamine and "Alkaloid C" in Table 1) different empirical formulas are put forward for the two bases, despite the extremely close data of their elementary analyses: $C_{28}H_{43}O_7N$ is given for the amino alcohol of delartine, and $C_{25}H_{39}O_7N$ for lycoctonine. Comparing the partially expanded formulas for the two alkaloids and replacing all the functional groups by hydrogen and the nitrogen by "CH" , we get the following expressions

TABLE 3

Constants	Amino alcohol of delartine	Lycoctonine	
		Schulze [9]	Goodson [4]
M.p. of the base (with a molecule of H_2O.....	110-115°	119-126°	119°
M.p. of the base (anhydrous).	137 -142°	137°	143°
Specific rotatory power.....	+56.6°	+49.64°	+53.2°
Functional groups.....	$(OCH_3)_4(OH)_3(NC_2H_5)$	$(OCH_3)_4(OH)_2(NCH_3)$	$(OCH_3)_4(OH)_3(NC_2H_5)$
M.p. of the hydrochloride....	With one molecule of H_2O: approx. 80°, anhydrous: 159-162°	75°	-
M.p. of the hydrobromide.....	With one molecule H_2O 89-91°, anhydrous 167-169°	88-89°	-
M.p of the hydriodide.....	174-176°	178° *	-
Per cent C.....	64.75 64.68	64.24 63.09	64.3
Per cent H.....	8.74 8.87	9.1 8.7	8.7
Per cent N.....	3.28 3.3	3.05	3.3
Empirical formula.....	$C_{28}H_{43}O_7N$	$C_{25}H_{39}O_7N$	$C_{25}H_{39}O_7N$

TABLE 4

Base	Partially expanded formula	Supposed heterocyclic ring	Hypothetical hydrocarbon
Amino alcohol of delartine.....	$C_{20}H_{23}(OH)_3(OCH_3)_4(NC_2H_5)$	$C_{20}H_{31}N$	$C_{21}H_{32}$
Lycoctonine.....	$C_{19}H_{19}(OH_3)(OCH_3)_4(NC_2H_5)$	$C_{19}H_{27}N$	$C_{20}H_{28}$

(Table 4).

Hence, provided no double bond is present (no such bond was found in an Adams hydrogenation), the amino alcohol of delartine ought to be a derivative of the hypothetical hydrocarbon $C_{21}H_{32}$, consisting of six hydrogenated rings, whereas lycoctonine must be a derivative of the hypothetical hydrocarbon $C_{20}H_{28}$, consisting of seven hydrogenated rings. The latter assumption seems to us to contradict the available data on the possible structure of aconite alkaloids. This cannot fail to recall the recent papers by the American researchers Walter Jacobs and Lyman Craig on the structure of aconite alkaloids. These authors have established the fact that atisine belongs to the phenanthrene series [11] and that staphisine [12] and napelline [13] likewise possess phenanthrene skeletons. It has been proved that the polymethylphenanthrene of staphisine is pimanthrene [14]; this established the relationship between the aconite alkaloids and the diterpenes. And, lastly, (what is of special importance), these research workers discovered (by the methods of spectrum analysis) that aconite alkaloids have conjugated double bonds, which are not revealed by the usual hydrogenation methods [15]. This leads these authors to suggest

* As against the statements of Schulze, we have established that the action of CH_3I upon the base produces the hydriodide, and not the iodomethylate.

that the basis of this group of alkaloids is a four-ring system, and not a six-ring system.

Howsoever that may be, the problem of the structure of the aconite alkaloids is so complicated that for the present we shall have to confine ourselves to hypotheses and suppositions regarding the possible nature of their basic ring systems.

In conclusion, we wish to express our thanks to our senior scientific associate, E.I.Miklashevska, candidate of chemical science, and her co-workers, who performed all the necessary analytical determinations.

EXPERIMENTAL

1. Recovery and Separation of the Alkaloids

10 kg of the ground-up plant was wetted with 5% ammonia and exhaustively extracted with dichloroethane. The dichloroethane extract was in turn extracted, first with 10% and then with 5% sulfuric acid; the acid solution was alkalized with 25% ammonia and then extracted; first with ether and then with chloroform. After the ether had been driven off, there remained 41 g of total alkaloids as a dark, hyaline mass; after the chloroform had been driven off, there remained an alkaloid mixture in the form of a hyaline mass again, weighing 11 g; the aggregate alkaloids totaled 0.52% of the dry plant weight.

The alkaloid mixture obtained from the ether extract was triturated into an amorphous, yellowish powder, which is soluble with difficulty in ether and readily soluble in ethyl acetate and in alcohol. Endeavors to recrystallize the base met with no success; an amorphous substance without a sharp melting point was recovered from the usual organic solvents.

2. Delphamine

The alkaloid mixture recovered from the chloroform fraction as a thick, hyaline mass was dissolved in 5% hydrochloric acid. The aqueous acid solution was washed with ether and benzene, after which it was alkalized with 25% ammonia and extracted with ether and chloroform. This caused a negligible proportion of the alkaloids to enter into ether solution, most of them being extracted with the chloroform. After the latter had been driven off, there remained a thick oil, which, after being triturated with acetone, turned into a yellowish powder that was hardly soluble in alcohol and in chloroform. When recrystallized from a mixture of absolute alcohol and ether, it separated out as lustrous orthogonal crystals with a m.p. of 190-196°. The base was purified via the tartrate: 0.1 g of the alkaloid was mixed with 0.03 g of tartaric acid in 1 ml of absolute alcohol; everything entered solution upon heating. After chilling, the tartrate crystallized out, with a m.p. of 157-161° (with decomposition); a test sample mixed with the tartrate of delphamine exhibited no depression. The base recovered from the tartrate fused at 195-198°.

0.1 g substance; 15 ml of absolute alcohol; $\underline{l} = 10$;
$\alpha = +0.36°$; $[\alpha]_D = +54°$.

0.1060 g substance: 15 ml 0.5 N HCl; $\underline{l} = 10$;
$\alpha = +0.24°$; $[\alpha]_D = +34°$.

Chloroaurite. A 10% solution of gold chloride is added drop by drop to a solution of delphamine in 5% hydrochloric acid; an oil separates out, which solidifies upon standing. It triturates to an orange powder. Recrystallized from dilute alcohol, it has a m.p. 171-172° (with decomposition).

3. Delartine

The alkaloid mixture recovered from the ether fraction is dissolved in 5% hydrochloric acid, and the acid solution is repeatedly washed with ether and benzene. A saturated aqueous solution of sodium perchlorate is added to the transparent, slightly colored, acid solution, causing the perchlorate of the base to settle out as a tarry, sticky mass, which is hard to dissolve in water, but dissolves readily in alcohol. Repeated trituration with soda and alcohol changes the perchlorate into a powder, which can be recrystallized from aqueous alcohol: 1 g of the perchlorate recrystallizes from a mixture of 15 ml of alcohol and 5 ml of water; when filtered, it recrystallizes instantaneously as minute needles, collected into clusters. The twice recrystallized perchlorate, which is entirely colorless, fuses at 188-190°. It contains 1.5 mols of water of crystallization, which is lost when the crystals are heated to 120° in vacuum.

0.0476 g substance: 12 ml dilute alcohol; $\underline{l}$ = 10.05.
α = + 0.1°; $[\alpha]_D$ = + 25.08°.
3.624 mg substance: 7.247 mg CO_2; 2.208 mg H_2O.
3.751 mg substance: 7.523 mg CO_2; 2.350 mg H_2O.
7.030 mg substance: 0.249 ml N_2 (22°, 736 mm).
7.210 mg substance: 0.258 ml N_2 (19.5°, 747 mm).
13.615 mg substance: 2.380 mg AgCl.
13.750 mg substance: 2.485 mg AgCl.
Found %: C 54.50, 54.69; H 6.81, 7.02; N 3.91, 4.10. Cl 4.32, 4.47.
$C_{36}H_{53}O_{11}N_2 \cdot HClO_4$. Calculated %: C 54.71; H 6.8; N 3.49; Cl 4.3.

The base is isolated from its perchlorate by triturating the latter with concentrated ammonia in the presence of ether; this causes the base to dissolve in the ether gradually. When the latter has been driven off, we again get a transparent, hyaline, lightly colored substance, which can be triturated to a light, amorphous powder, m.p. 110-130°.

0.1498 mg substance: 13 ml alcohol; $\underline{l}$ = 10.0.
α = + 0.52; $[\alpha]_D$ = + 45.1°.

4. Saponification of Delartine

5 g of delartine perchlorate is boiled for 3 hours with 50 ml of an alcoholic 10% solution of potassium hydroxide. After the alcohol has been driven off, 5-7 ml of water is added to the syrupy base, causing all of it to turn into a crystalline mass. The amino alcohol is separated out on a suction filter, washed with water, dissolved in 10 ml of 5% hydrochloric acid, and precipitated by adding 10% ammonia, after which 2.5 g of the snow-white, crystalline base is recovered on a suction filter. It is recrystallized from 20% aqueous alcohol as beautiful, acicular crystals, m.p. 110-115°.

0.2060 g substance: 12 ml alcohol; 10.05.
α = + 0.92°; $[\alpha]_D$ = + 53.3.
3.708 mg substance: 8.548 mg CO_2; 2.944 mg H_2O.
2.810 mg substance: 6.456 mg CO_2; 2.202 mg H_2O.
7.745 mg substance: 0.215 ml N_2 (22°, 737 mm).
7.345 mg substance: 0.198 ml N_2 (22°, 736 mm).
14.860 mg substance: 2.65 ml CH_4 (0°, 760 mm).
13.770 mg substance: 2.44 ml CH_4 (0°, 760 mm).
22.90 mg substance: 11.07 ml 0.01 N $Na_2S_2O_3$.
15.40 mg substance: 7.37 ml 0.01 N $Na_2S_2O_3$.
0.2110 g substance: 4.25 0.1 N HCl (methyl red)

Found %: C 62.87, 62.66; H 8.88, 8.77; N 3.12, 3.02.
OH 13.62, 13.54; OCH_3 24.99, 24.74. M 496.
$C_{28}H_{43}O_7N \cdot H_2O$. Calculated %: C 62.52; H 9.01; N 2.8; 4OH 13.62; 4 OCH_3 24.84; M 499.

The amino alcohol, desiccated in vacuum at 120° to constant weight, turns into a yellowish, hyaline substance. Its m.p. is 142-145° after recrystallization from benzene.

3.564 mg substance: 8.460 mg CO_2; 2.785 mg H_2O.
4.259 mg substance: 10.101 mg CO_2; 3.377 mg H_2O.
8.525 mg substance: 0.252 ml N_2 (24°, 734.5 mm).
9.330 mg substance: 0.275 ml N_2 (22.5°, 736.5 mm).
16.085 mg substance: 2.27 ml CH_4 (0°, 760 mm).
Found %: C 64.75, 64.68; H 8.74, 8.87; N 3.28, 3.30.
OH 10.78.
$C_{28}H_{43}O_7N$. Calculated %: C 64.86; H 8.93; N 2.9; 3OH 10.6.

5. Salts of the Amino Alcohol

Hydrobromide. 0.5 g of the amino alcohol is mixed with 3-5 ml of acetone and 5-7 ml of hydrobromic acid, diluted with acetone. Everything dissolves at once, and the solution crystallizes when rubbed with a glass rod. The hydrobromide is recrystallized from a mixture of acetone and absolute alcohol. Minute, acicular colorless crystals, with a m.p. of 89-91°. M.p. 167-169 ° (with decomposition) after drying to constant weight.

Hydrochloride. This is prepared by mixing alcoholic solutions of the amino alcohol and hydrochloric acid. After the alcohol has been driven off in vacuum and the residual syrup is triturated with acetone, it turns into a crystalline powder. It is recrystallized from a mixture of absolute alcohol and ether. It decomposes at a temperature of about 80°. It fuses at 159-162° after having been dried to constant weight.

4.875 mg substance: 1.390 mg AgCl.
5.220 mg substance: 1.429 mg AgCl.
Found %: Cl 7.05, 6.77.
$C_{28}H_{43}O_7N \cdot HCl$. Calculated %: Cl 6.86.

Perchlorate. A saturated aqueous solution of sodium perchlorate is added to a solution of the amino alcohol in 5% hydrochloric acid. The resulting transparent solution is evaporated, the syrupy residue is treated with absolute alcohol, and the alcoholic solution is evaporated to dryness in vacuum. The residue is recrystallized from a mixture of absolute alcohol and ether. Colorless needles. Fuses at 87-90° with foaming.

Hydriodide. 0.1 g of amino alcohol is mixed with 2-3 ml of acetone, and a few drops of colorless hydriodic acid are added; the ingredients dissolve at once, and rubbing converts the whole into a crystalline mass. This yielded 0.11 g of the hydriodide; it is recrystallized from a mixture of acetone and alcohol, with a few drops of absolute ether added. Lustrous needles. The hydriodide, desiccated in vacuum at 120°, fuses at 174-176° (with decomposition).

5.245 mg substance: 5.22 ml 0.01 N $Na_2S_2O_3$.
5.745 mg substance: 5.67 ml 0.01 N $Na_2S_2O_3$.
Found %: I 21.0, 20.88.
$C_{28}H_{43}O_7N \cdot HI$. Calculated %: I 20.8.

6. Action of Methyl Iodide

0.5 g of the amino alcohol is dissolved in 5 ml of methanol, and 1 ml of methyl iodide is added with chilling; the solution is heated for three hours in a

sealed tube, over a water bath. After cooling, the contents of the tube are evaporated to dryness. The residue was repeatedly treated with hot ether, after which it was recrystallized from a mixture of alcohol and ether; beautiful golden needles, m.p. 176-178° (with decomposition).

The addition of a few drops of 25% ammonia to an aqueous solution of the synthesized substance causes the base to crystallize; it proves to be identical with the initial amino alcohol.

A test sample of the product of the action of CH_3I upon the amino alcohol exhibited no depression when mixed with the hydriodide.

8.070 mg substance: 8.066 ml 0.01 N $Na_2S_2O_3$.
6.990 mg substance: 7.000 ml 0.01 N $Na_2S_2O_3$.
Found %: 21.14, 21.19.
$C_{28}H_{43}O_7N \cdot HI$. Calculated %: N 20.8.

7. Oxidation of the Amino Alcohol

A solution of 0.31 g of potassium permanganate in 10 ml of water is added from a dropping funnel to a solution of 1 g of the amino alcohol in 8 ml of 1 N sulfuric acid, with chilling and stirring. After the solution is decolorized, the manganese dioxide is filtered out, and the light-yellow solution is distilled into a well-chilled receiver. 50 ml of a 1% aqueous solution of dimedon; when the solution was heated, it turned cloudy after a few minutes, and a light, finely crystalline precipitate settled out. 0.05 g of the substance separated out on a suction filter; it was recrystallized from 2 ml of petroleum ether (b.p. 24-40°), after which it fused at 132-134°. The condensation product of dimedon with acetaldehyde fuses at 138-139°, the mixed test sample fusing at 134-137°.

8. Endeavor to Hyrdrogenate the Amino Alcohol

An Adams platinum catalyst was prepared from 0.7 g of a mixture of platinic chloride and saltpeter. The platinum oxide was reduced in 10 ml of concentrated acetic acid. After the platinum oxide had been reduced, 0.4 g of the amino alcohol was added to the acetic-acid solution, and the solution was shaken for 3 hours in hydrogen, no hydrogen being absorbed. After the catalyst was filtered out, the solution was evaporated in vacuum, 3-4 ml of water was added to the resulting syrupy residue, and the acetic-acid solution was alkalized with 25% ammonia; this resulted in the immediate crystallization of the initial amino alcohol.

9. Delartinic Acid

The alkaline aqueous solution, from which the crystalline amino alcohol is removed by filtration, is extracted with ether. After exhaustive removal of the residual amino alcohol, the aqueous solution is acidulated with 5% hydrochloric acid, the acid separating out as an oil, which turns into a coarse-grained, yellow mass upon standing. 2.5 g of delartinic acid, which dissolves with difficulty in water and readily in alcohol and ethyl acetate. It is purified by repeated treatment with cold ether. After the latter had been evaporated, there was left a yellow amorphous acid, which was recrystallized from a mixture of ether and ethyl acetate in the presence of charcoal. Yellowish, unsharp, amorphous grains, with a m.p. of 160-164° (with decomposition).

10. Saponification of Delartinic Acid

a) 1.5 g of delartinic acid was boiled with 15 ml of 10% hydrochloric acid for an hour and a half, all of the ingredients gradually dissolving. Upon cooling, the acid, slightly colored, aqueous solution was extracted with ether. The nearly colorless ether solution was desiccated with sodium sulfate and evaporated to a small

volume, from which 1 g of a slightly tinted substance with a m.p. of 140-141° was crystallized. Recrystallization from 3 ml of water yielded minute needles, m.p. 143-145°. They exhibited no depression when mixed in a test sample with anthranilic acid.

4.051 mg substance: 9.141 mg CO_2; 1.771 mg H_2O.
3.677 mg substance: 8.290 mg CO_2; 1.647 mg H_2O.
6.120 mg substance: 0.540 ml N_2 (20.8°, 741 mm).
4.790 mg substance: 0.429 ml N_2 (20°, 741.2 mm).
Found %: C 61.54, 61.48; H 4.89, 5.01; N 10.01, 10.16.
$C_7H_7O_2N$. Calculated %: C 61.3; H 5.1; N 10.2.

b) The aqueous acid solution, from which the anthranilic acid had been removed by extraction with ether, was evaporated to dryness; the residue consisted of 0.5 g of a yellow crystalline acid. Soluble with very great difficulty in ether or acetone; readily soluble in water or alcohol. It was recrystallized from a mixture of acetone and alcohol; when ether was added, colorless needles with a m.p. of 170-176° crystallized out. The acid sublimes in vacuum at 140-150° as colorless needles with a m.p. of 170-172° (with decomposition).

SUMMARY

1. Two alkaloids have been isolated from Delphinium sp., which grows in the Central Tian Shan, near the Kyz-Art Pass: one of them, crystalline, was found to be identical with delphamine; the other, a new noncrystalline alkaloid, has been named delartine.

2. Alkaline hydrolysis of delartine yielded a crystalline amino alcohol and a noncrystalline, nitrogen-containing acid, which has been named delartinic acid.

3. In all its properties, the amino alcohol of delartine resembles lycoctonine, and it may therefore be assumed that they are identical.

4. Saponification of delartinic acid yielded two crystalline substances, one of which proved to be anthranilic acid.

5. The "Alkaloid C" isolated by Goodson [6] from Delphinium ajacis may be identical with the delphamine previously isolated by us from Delphinium sp. [1]

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THE ALKALOIDS OF AMMODENDRON CONOLLYI BGE.

II. THE ISOLATION OF THE NEW ALKALOIDS: ISOAMMODENDRINE AND CONOLLINE

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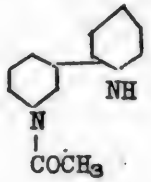
In our first paper [1] on the alkaloids of Ammodendron Conollyi Bge (Leguminosae family), we reported the isolation of two alkaloids from this plant: the previously described pachycarpine $C_{15}H_{26}N_2$ and the new alkaloid ammodendrine $C_{12}H_{20}N_2O$. We demonstrated that dihydroammodendrine (I) is a monoacetyl derivative of α,β-dipiperidyl, the acetyl group lying in the beta-substituted ring:



Final elucidation of the structure of ammodendrine required merely the determination of where the double bond was located in its molecule.

In the continuation of our research on the Ammodendron Conollyi of one of the 1936 harvests,* we observed important divergencies from our previous experiments while distilling the total alkaloids in vacuum to separate the pachycarpine from the ammodendrine by the established method, namely: the second fraction, which passed over in the 175-200° (4 mm) range, remained liquid, though it usually consists of crystalline ammodendrine, and the hydriodide derived from it had laevorotation.

As ammodendrine is an optically inactive substance, we supposed that the crystallization of the second fraction was interfered with by a trace of some other alkaloid, which was evidently laevorotatory. In order to isolate this alkaloid, we refrained from distilling the total alkaloids, fearing this might involve the decomposition of some unknown substance; we used a milder method of separating the alkaloids by converting them into their hydriodides.

The above-mentioned pachycarpine and ammodendrine (only an extremely small quantity of the latter), as well as three other alkaloids, were recovered from the same plant by this method. One of them rotates the plane of polarization to the left and is a hyaline, amorphous mass. We identified it as the previously [2] described anagyrine $C_{15}H_{20}N_2O$ by directly comparing their salts, the most characteristic of which were the perchlorate (m.p. 270-271° with decomposition), the picrate (m.p. 242-243°), and the iodomethylate (m.p. 263-264°).

Anagyrine has also been described as an amorphous, hyaline substance, and it has not yet been prepared in crystalline form. All the other properties of the alkaloid that we have isolated likewise agree with the properties of anagyrine: its ready solubility in the usual organic solvents, except for petroleum ether; its higher solubility in cold water than in hot; its b.p. of 210-220° (4-5 mm); and

*In 1936 two crops of the plant Ammodendron Conollyi were harvested: at the beginning of July and in September.

its $[\alpha]_D$ of -165.3° in alcoholic solutions.

The second alkaloid isolated by us crystallizes from alcohol with a m.p. of 192.5-193.5°. Its composition is closest to $C_{13}H_{20}N_2O$; it contains no hydroxyl or methoxyl groups. In its properties and composition, this alkaloid differs from all those hitherto described, and we have named it conolline. It does not decolorize permanganate in sulfuric acid, hence, it is a saturated compound. It is optically inactive. Its most characteristic salt is the perchlorate, which is extremely poorly soluble in water as well as in all other solvents. When conolline was heated with an alcoholic alkali, it was recovered unchanged. We were unable to isolate conolline by vacuum distillation to separate the total alkaloids. We recovered it from the mother liquors left after the principal alkaloids had been isolated as a mixture of crystalline hydriodides. The percentage of conolline in the plant is extremely slight (0.007%); this hampers its detailed examination considerably.

The percentage of the third, new alkaloid isolated by us in the plant is fairly high (approximately 0.1%). Its composition fits the formula $C_{12}H_{20}N_2O$, and hence it is an isomer of ammodendrine. We have named it isoammodendrine. Isoammodendrine contains no hydroxyl, methoxyl, or methylimide groups. It is extremely hygroscopic, so that we were able to obtain it in crystalline form only after redistillation in vacuum and prolonged storage in a vacuum exsiccator. In air, isoammodendrine begins to deliquesce immediately, but it does not exhibit a crystallohydrate form, wherein it differs from ammodendrine. After recrystallization from anhydrous petroleum ether, isoammodendrine fuses somewhere in the neighborhood of 43-46°; its $[\alpha]_D$ = + 15.9° in alcoholic solution. All its salts, such as the hydrochloride, the hydriodine, and the perchlorate, are laevorotatory, and their melting points are extremely close to those of the corresponding salts of ammodendrine; no depression of the melting points was observed in mixed test samples. Isoammodendrine, like ammodendrine, is unsaturated, as it does not decolorize permanganate in sulfuric acid. When it is heated with alkalies, acetic acid is detached; hence, its expanded formula may be written as follows:

$$C_{10}H_{17}N\cdot(NCOCH_3).$$

All these facts testify to the close link between isoammodendrine and ammodendrine; the idea therefore suggests itself that they may be optical isomers. The research on the structure of isoammodendrine is being continued.

It is worthy of note that the ratio between the percentages of ammodendrine and isoammodendrine fluctuates widely in plants collected at various times. In some, ammodendrine is the principal alkaloid, only a trace of the isoammodendrine being present, as was found during an examination of the raw material of the 1935 crop (Kara-Kum). In other cases, the isoammodendrine is the principal alkaloid, with only a trace of the ammodendrine present (1936 crop). The reasons underlying these fluctuations will probably be learned only after a thorough study of the dynamics of the accumulation of the alkaloids in the plant as affected by various factors. The time of harvest most likely plays an important part in this regard, though it is possible that only the soil and climactic peculiarities of the plant's habitat are the determinant factors.

EXPERIMENTAL

31 kg of the air-dried, finely ground leaves of Ammodendron Conollyi were wetted with 5% ammonia and extracted with dichloroethane until extraction was complete. The dichloroethane was extracted in turn with 10% sulfuric acid. The combined acid extracts were alkalized with ammonia, desiccated with potash, and extracted 12 times with sulfuric ether, and then with chloroform. The ether extract was desiccated with calcined potash. Driving off the ether yielded 186 g of total alkaloids as a dark-yellow liquid oil (0.6%). Driving off the chloroform yielded 291 g of total alkaloids as a dark-brown sticky, tarry mass (0.9%).

Separating the Total Alkaloids Recovered from the Ether Extract

1. Isolating Pachycarpine and Isoammodendrine as Crystalline Hydriodides

Hydriodic acid was added to 186 g of the total alkaloids dissoved in 100 ml of alcohol until the reaction with Congo red was slightly acid. When the solution was stirred, the crystalline hydriodide precipitated out. The next day, the precipitate was removed on the suction filter and washed with acetone. This yielded 182 g of a yellow mixture of hydriodides.

a) Separation of pachycarpine and isoammodendrine. The mixture of hydriodides was dissolved in water, with heating, and the aqueous solution was extracted with chloroform after having been alkalized with sodium hydroxide. The chloroform extract was desiccated over anhydrous sodium sulfate. Driving off the chloroform yielded 95 g of the bases, which were then distilled in vacuum. Two fractions were collected: 48.6 g of the first, passing over at 165-175° (8-9 mm); and 38.9 g of the second, passing over at 175-186° (8-9 mm). The residue, not distillable at this temperature, was 5.8 g.

The first fraction consists of pachycarpine [1]. The second fraction was redistilled, after which it yielded a hydriodide with a m.p. of 218-219° and an $[\alpha]_D$ of -17.5°. Further recrystallization effected no changes in the melting point or the specific rotatory power.

b) Isolation of isoammodendrine. The hydriodide was dissolved in water, with heating. The aqueous solution was extracted with ether after having been alkalized with sodium hydroxide and saturated with potash. After the ether extract had been desiccated over sodium sulfate and the solvent had been driven off, isoammodendrine was recovered as a thick, light-yellow, noncrystallizing oil, which distilled in vacuum without decomposition at 174-180° (5-6 mm). After redistillation in vacuum and standing for a long time in a vacuum exsiccator, the colorless, thick base crystallized. It fused, not sharply, at 38-43°. Recrystallization from anhydrous petroleum ether (lower boiling fraction) yielded large crystals with an unsharp m.p. of 43-46°, which deliquesce quickly in air. Isoammodendrine is readily soluble in alcohol, acetone, benzene, and chloroform., fairly readily in water, less so in cold ether, and with great difficulty in petroleum ether. It decolorizes permanganate instantaneously in sulfuric-acid solution.

1.1806 g substance: 12 ml alcohol; $\underline{l} = 1$; α_D +1.56°; $[\alpha]_D$ + 15.9°.
4.190 mg substance: 10.624 mg CO_2; 3.590 mg H_2O.
4.020 mg substance: 10.198 mg CO_2; 3.450 mg H_2O.
3.085 mg substance: 0.352 ml N_2 (20°, 739 mm).
3.510 mg substance: 0.420 ml N_2 (24°, 717 mm).
Found %: C 69.15, 69.19; H 9.59, 9.60; N 12.93, 12.98.
$C_{12}H_{20}ON_2$. Calculated %: C 69.23; H 9.61; N 13.46.

0.2245 mg substance: 10.75 ml 0.1 N HCl (methyl red).
Found: M 208.8.
$C_{12}H_{20}ON_2$. Calculated: M 208.

Isoammodendrine hydrochloride. Alcoholic hydrochloric acid was added to 1 g of the base dissolved in 5 ml of anhydrous acetone until the reaction was neutral. Rubbing caused a finely crystalline deposit to settle out, with a m.p. of 192-193°. This latter is very highly soluble in water and in alcohol. It dissolves readily enough in chloroform, but is insoluble in acetone. The m.p. was 193-194° after recrystallization from an alcohol-acetone mixture.

0.313 g substance: 10 ml water; $\underline{l} = 0.947$; α_D -0.8°; $[\alpha]_D$ -27.4°.

3.274 mg substance: 7.044 mg CO_2; 2.538 mg H_2O.
3.874 mg substance: 8.388 mg CO_2; 3.018 mg H_2O.
2.593 mg substance: 0.255 ml N_2 (18°, 749 mm).
2.547 mg substance: 0.249 ml N_2 (18°, 747 mm).
3.550 mg substance: 2.185 mg AgCl.
3.720 mg substance: 2.265 mg AgCl.

Found %: C 58.68, 58.70; H 8.67, 8.72; N 11.20, 11.10; Cl 15.23, 15.06.

$C_{12}H_{20}ON_2 \cdot HCl$. Calculated %: C 58.85; H 8.65; N 11.44; Cl 14.91.

A test sample mixed with an ammodendrine hydrochloride whose m.p. was 207° fused at 196-197°.

Ammodendrine hydrochloride was prepared, for the sake of comparison, in the same way as the isoammodendrine hydrochloride. M.p. 207-208°. Optically inactive.

Hydriodide. Hydriodide acid was added to 0.5 g of the base dissolved in 5 ml of alcohol. Recrystallization from hot water (approximately 1:5) yielded the hydriodide as transparent, colorless crystals with a m.p. of 218-219°. It dissolves with some difficulty in alcohol and is insoluble in acetone; it is fairly readily soluble in chloroform. A test sample, mixed with ammodendrine hydriodide, with a m.p. of 217-218°, fused at 218-219°.

0.4 g substance: 10 ml water; l = 0.947; α_D - 0.8°; $[\alpha]_D$ - 21.1°.

Perchlorate. A saturated aqueous solution of sodium perchlorate was added to an aqueous hydrochloric-acid solution of the base. A crystalline precipitate, with a m.p. of 198-200°, settled out immediately. Recrystallization from hot water (1:6) caused crystals as short prisms with a m.p. of 202-203° to separate out gradually. A test sample mixed with an ammodendrine perchlorate that had a m.p. of 199-200° fused at 201-202°.

0.145 g substance: 10 ml water; l = 0.947; α_D - 0.3°; $[\alpha]_D$ - 21.9°.

Saponification of isoammodendrine by alcoholic potassium hydroxide. 0.5 g of the base was heated with a solution of 1.75 g of KOH in 5 ml of methyl alcohol for 6 hours with reflux condenser over a water bath. The alcohol was driven off in vacuum; the residue - a yellow, oily substance - was diluted with 3 ml of water and extracted with ether. Driving off the ether yielded a yellow oil that did not form any crystalline salts. Phosphoric acid was added to the alkaline solution, diluted with water, and then the acid solution underwent distillation. The aqueous acid distillate was neutralized with 0.1 N NaOH and concentrated down to small volume; then a silver-nitrate solution was added to it. The precipitated silver salt was filtered out by suction, washed with water, and recrystallized from water.

0.1601 g substance: 0.1033 g Ag.

Found %: Ag 64.54.

$C_2H_3O_2Ag$. Calculated %: Ag 64.64.

2. Analysis of the Mother Liquors Left After Isolating the Pachycarpine and Isoammodendrine as their Hydriodides

a) Isolating conolline. After the alcohol had been removed from the dark-colored mother liquor, it was alkalized with a solution of sodium hydroxide, saturated with potash, and exhaustively extracted with ether. Upon standing, conolline gradually crystallized from the ether solution as a white, finely crystalline substance. The yield of conolline was 2.3 g (0.007%), with a melting point of 192.5-193.5° after recrystallization from alcohol.

Conolline is very readily soluble in chloroform and readily soluble in hot alcohol, but soluble with difficulty in cold; it dissolves with difficulty in sulfuric

and petroleum ether and is nearly insoluble in water. It crystallizes best from alcohol, as minute prisms. Conolline does not decolorize permanganate in sulfuric-acid solution. It is optically inactive.

2.976 mg substance: 7.767 mg CO_2; 2.521 mg H_2O.
3.630 mg substance: 9.451 mg CO_2; 3.106 mg H_2O.
5.097 mg substance: 0.5822 ml N_2 (23.5°, 728 mm).
5.364 mg substance: 0.616 ml N_2 (23.0°, 730 mm).
Found %: C 71.17, 71.01; H 9.47, 9.57; N 12.6, 12.72.
$C_{13}H_{20}ON_2$. Calculated %: C 70.86; H 9.15; N 12.7.

Hydrochloride. Alcoholic hydrochloric acid was added to a hot solution of 0.1 g of conolline in 3 ml of acetone. A resinous white precipitate settled out, which turned crystalline after standing for two days. After suction-filtering and washing with acetone, the not entirely pure crystalline substance was redissolved in 1 ml of alcohol, and 2 ml of acetone was added to the solution. A resinous precipitate settled out again; upon standing it turned crystalline, with an unsharp m.p. of 180-182°. It is very highly soluble in water and in alcohol, but is insoluble in acetone. It deliquesces in air upon standing.

Perchlorate. When a saturated aqueous solution of sodium perchlorate was added to a neutral solution of the base in 5% hydrochloric acid, conolline-perchlorate settled out as a white resin, which crystallized quickly when rubbed. M.p. 194-195°. It dissolves with extremely great difficulty in water, alcohol, acetone, and other solvents. The m.p. is 197-198° after recrystallization from a large quantity of hot water.

Hydriodide. Adding hydriodic acid to an alcoholic solution of conolline yields the hydriodide, which crystallizes only upon standing. M.p. 195-196°.

Hydrobromide. Adding hydrobromic acid to an alcoholic solution of conolline does not cause the hydrobromide to precipitate out. Drying changes the whole into a hyaline mass.

b) Isolating anagyrine. 47.5 g of a mixture of bases with a specific rotatory power of $[\alpha]_D$ -34.4° was recovered from the ether extract after the conolline had been separated out and the ether driven off.

The whole mixture of bases was dissolved in 150 ml of chloroform, and the chloroform solution was extracted with ten 20.4-ml batches of 1 N sulfuric acid. All the ten fractions were highly colored. Each fraction was neutralized and evaporated to small volume, after which it was saturated with potash and extracted with ether. After the ether had been driven off, we measured the specific rotatory power of the base isolated from each fraction, the laevorotation increasing with every fraction above the fourth. The 1st, 2nd, and 3rd fractions consisted of pachycarpine. Their picrates fused at 202°, and a test sample mixed with pachycarpine picrate exhibited no depression of the melting point. Pachycarpine and isoammodendrine were recovered from the 4th, 5th and 6th fractions. The perchlorate was prepared from the 7th, 8th, 9th, and 10th fractions, which had $[\alpha]_D$ ranging from -84° to -127.9°. After repeated fractional recrystallization from hot water, the perchlorate consisted of fine, interlaced needles, which settle out as soon as the solution begins to cool. The temperature of decomposition is 270-271°. A test sample mixed with anagyrine that fuses at 271-272° exhibited no depression. Isoammodendrine perchlorate was recovered from the aqueous liquors left after crystallization of the anagyrine perchlorate; the former's solubility in water is almost the same as that of anagyrine perchlorate, but it does not settle out at once when the solution is chilled.

To isolate the base, the perchlorate with a decomposition temperature of 270-

271° was dissolved in warm water, alkalized with ammonia, and extracted with ether; driving off the latter yielded a yellow, extremely thick oil, which decolorizes permanganate in sulfuric-acid solution instantaneously, and turns red and changes into a hyaline mass upon standing. The base, distilled in vacuum at 215-220° (5 mm), had a $[\alpha]_D$ of -165.3°.

Picrate. When an alcoholic solution of picric acid was added to an alcoholic solution of the base, a yellow precipitate was thrown down; it was isolated as fine, yellow, lustrous needles with a m.p. of 242-243° after recrystallization from a mixture of alcohol and acetone. A test sample mixed with anagyrine picrate that had a m.p. of 243° exhibited no depression.

Treatment of the Chloroform Fraction

291 g of the dark brown resin was treated five times with 500 ml of boiling sulfuric ether. Driving off the ether yielded 79 g of a light-yellow base (0.25% of the plant by weight) with $[\alpha]_D$ -14.2°. The whole base was converted into a resinous hydriodide, which fused at 218-219° and had $[\alpha]_D$ -16.9°, after washing with acetone and recrystallization from water with activated charcoal. Isoammodendrine hydriodide with $[\alpha]_D$ -21.1° was isolated after 3 recrystallizations from water. Ammodendrine hydriodide, with $[\alpha]_D \doteq 0$ was recovered from the aqueous mother liquors.

The alcoholic mother liquor left after recovery of the hydriodide was combined with the residue left after the wash acetone was driven off. Alkalization with ammonia yielded a base with $[\alpha]_D$ of -82.1°, the perchlorate of which was prepared. The perchlorate had a m.p. of 270-271° after repeated recrystallization from water. A test sample mixed with anagyrine exhibited no depression (270-271°).

SUMMARY

1. Three alkaloids: anagyrine and 2 new alkaloids, which have been named isoammodendrine and conolline, have been found in the Central Asian plant Ammodendron Conollyi Bge., in addition to the pachycarpine and ammodendrine isolated previously.

2. It has been learned that plants gathered at different times contain either ammodendrine with a trace of isoammodendrine or isoammodendrine with a trace of amodendrine.

3. Isoammodendrine has the minimum formula $C_{12}H_{20}ON_2$ and is an unsaturated base. Its expanded formula is $C_{10}H_{17}N(NCOCH_3)$. Its salts are laevo rotatory.

4. Conolline has the minimum formula $C_{13}H_{20}ON_2$. Its percentage in the plant is extremely low.

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